

INSTITUTE OF METALS
DIVISION

1942

A. I. M. E.

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TRANSACTIONS

vol 147
N/C
OF THE

AMERICAN INSTITUTE OF MINING
AND METALLURGICAL ENGINEERS

(INCORPORATED)

and Petroleum

Volume 147

INSTITUTE OF METALS DIVISION
1942

PAPERS AND DISCUSSIONS PRESENTED BEFORE THE DIVISION AT MEETINGS HELD AT
PHILADELPHIA, OCTOBER 20-22, 1941, AND NEW YORK,
FEBRUARY 9-12, 1942

PUBLISHED BY THE INSTITUTE
AT THE OFFICE OF THE SECRETARY

29 WEST 39TH STREET
NEW YORK, N. Y.

Notice

This volume is the sixteenth of a series constituting the official proceedings of the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers. It deals with nonferrous metals and includes papers presented at the Philadelphia Meeting, Oct. 20-22, 1941, and the New York Meeting, Feb. 9-12, 1942. The complete list of publications and proceedings, including the present volume, is as follows:

- 1908-1911 *Transactions* of the American Brass Founders' Association: 1908, Vols. 1 and 2; 1909, Vol. 3; 1910, Vol. 4; 1911, Vol. 5.
- 1912-1916 *Transactions* of the American Institute of Metals, Vols. 6-10.
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- 1919-1926 TRANSACTIONS of the American Institute of Mining and Metallurgical Engineers, Volumes 60, 64, 67, 68, 69, 70, 71 and 73.
- 1927-1928 PROCEEDINGS of the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers, two volumes, of which the later is now designated Vol. 78 of the A. I. M. E. TRANSACTIONS.
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PRINTED IN THE UNITED STATES OF AMERICA

THE MAPLE PRESS COMPANY YORK, PA.

FOREWORD

This volume of the TRANSACTIONS of the American Institute of Mining and Metallurgical Engineers, containing papers presented before the Institute of Metals Division, adds a series of high-grade papers on the science and practice of Physical Metallurgy to the valuable contributions of previous volumes. Under the able guidance of Mr. E. E. Schumacher and his Papers and Programs Committee, the Division has enjoyed a splendid series of technical sessions.

This permanent record and its predecessors will serve as a guide to ways of solution of many of the perplexing problems confronting metallurgists, as the struggles for increased production, for improved quality, and for new alloys with new properties continue in our effort to fill the needs of our armed forces in the present national emergency.

The annual lecture this year was given by Mr. William Reuben Webster, a pioneer in applying the science of metals to the production of wrought brass products. In future years this lecture, "Notes on the History, Manufacture, and Properties of Wrought Brass," will serve as a primary source for the brass-mill metallurgy and practice of its day.

Membership and interest in Division affairs continue at a high level, owing in no small measure to the activity of the various committees. As Chairman of the Division, I would like to express my appreciation for the help and cooperation given me by these committees, by other officers of the Division, and by our Secretary, Mr. Frank Sisco, who has at all times kept the problems and welfare of the Division uppermost in his mind.

CARL E. SWARTZ, *Chairman*,
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Established as a Division April 26, 1918

(Bylaws published in the 1939 TRANSACTIONS Volume of the Division.)

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ANNUAL AWARD CERTIFICATE OF THE INSTITUTE OF METALS DIVISION

In 1933, the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers established its annual award of an engraved certificate to the author or authors of the paper that in the opinion of the award committee represents the most notable contribution to metallurgical science among the papers that have been accepted by the Division for presentation at one of its meetings and have been published by the Institute within the three years preceding the date of award. The award is made by the Division each February. There are no restrictions with respect to nationality, age or occupation of the author or authors.

Awards have been made as follows:

- 1934 Robert F. Mehl and Charles S. Barrett: Studies upon the Widmānstätten Structure, I—Introduction. The Aluminum-silver System and the Copper-silicon System. *TRANSACTIONS* (1931) **93**, 78-110.
- 1935 E. A. Anderson, M. L. Fuller, R. L. Wilcox and J. L. Rodda: The High-zinc Region of the Copper-zinc Phase Equilibrium Diagram. *TRANSACTIONS* (1934) **111**, 264-292.
- 1936 Cyril S. Smith and W. Earl Lindlie: A Micrographic Study of the Decomposition of the Beta Phase in the Copper-aluminum System. *TRANSACTIONS* (1933) **104**, 69-105.
- 1937 Arthur Phillips and R. M. Brick: Effect of Quenching Strains on Lattice Parameter and Hardness Values of High-purity Aluminum-copper Alloys. *TRANSACTIONS* (1934) **111**, 94-112.
- 1938 William L. Fink and Dana W. Smith: Age-hardening of Aluminum Alloys, I—Aluminum-copper Alloy. *TRANSACTIONS* (1936) **122**, 284-293.
- 1939 Frederick N. Rhines and Robert F. Mehl: Rates of Diffusion in the Alpha Solid Solutions of Copper. *TRANSACTIONS* (1938) **128**, 185-221.
- 1940 Alden B. Greninger: Martensite Transformation in Beta Copper-aluminum Alloys. *TRANSACTIONS* (1939) **133**, 204-221.
- 1941 S. E. Maddigan and A. I. Blank: Recovery and Recrystallization in Long-time Annealing of 70-30 Brass. *TRANSACTIONS* (1940) **137**, 170-190.
- 1942 F. N. Rhines: A Metallographic Study of Internal Oxidation in the Alpha Solid Solutions of Copper. *TRANSACTIONS* (1940) **137**, 246-288.

THE INSTITUTE OF METALS LECTURE

An annual lectureship was established in 1921 by the Institute of Metals Division, which has come to be one of the important functions of the Annual Meeting of the Institute. In 1934 the Division established the custom of presenting a certificate to each lecturer.

A number of distinguished men from this country and abroad have served in this lectureship. The roll is quoted below:

- 1922 Colloid Chemistry and Metallurgy. By Wilder D. Bancroft.
- 1923 Solid Solution. By Walter Rosenhain.
- 1924 The Trend in the Science of Metals. By Zay Jeffries.
- 1925 Action of Hot Wall: a Factor of Fundamental Influence on the Rapid Corrosion of Water Tubes and Related to the Segregation in Hot Metals. By Carl Benedicks.
- 1926 The Relation between Metallurgy and Atomic Structure. By Paul D. Foote.
- 1927 Growth of Metallic Crystals. By Cecil H. Desch.
- 1928 Twinning in Metals. By C. H. Mathewson.
- 1929 The Passivity of Metals, and Its Relation to Problems of Corrosion. By Ulick R. Evans.
- 1930 Hard Metal Carbides and Cemented Tungsten Carbide. By S. L. Hoyt.
- 1931 X-ray Determination of Alloy Equilibrium Diagrams. By Arne Westgren.
- 1932 The Age-hardening of Metals. By Paul D. Merica.
- 1933 Present-day Problems in Theoretical Metallurgy. By Georg Masing.
- 1934 Ferromagnetism in Metallic Crystals. By L. W. McKeehan.
- 1935 Gases in Metals. By C. A. Edwards.
- 1936 Diffusion in Solid Metals. By Robert F. Mehl.
- 1937 Refractories. By R. S. Hutton.
- 1938 The Nature of Metals as Shown by Their Properties under Pressure. By P. W. Bridgman.
- 1939 The Creep of Metals. By D. Hanson.
- 1940 Acceleration of Rate of Corrosion by High Constant Stresses. By Edgar H. Dix, Jr.
- 1941 Some Fundamentals of the Flow and Rupture of Metals. By George Sachs.
- 1942 Notes on the History, Manufacture, and Properties of Wrought Brass. By Wm. Reuben Webster.



WM. REUBEN WEBSTER
Institute of Metals Division Lecturer, 1942

Notes on the History, Manufacture and Properties of Wrought Brass

By Wm. REUBEN WEBSTER,* MEMBER A.I.M.E.

(Institute of Metals Division Lecture†)

BRASS is an alloy of copper and zinc. The brasses (using this term to denote all useful proportions of the two constituents) are the most valuable and widely employed of all

brass containing 70 per cent copper and 30 per cent zinc. Fig. 3 shows the effect of annealing at various temperatures on the same alloy. This effect is somewhat modi-

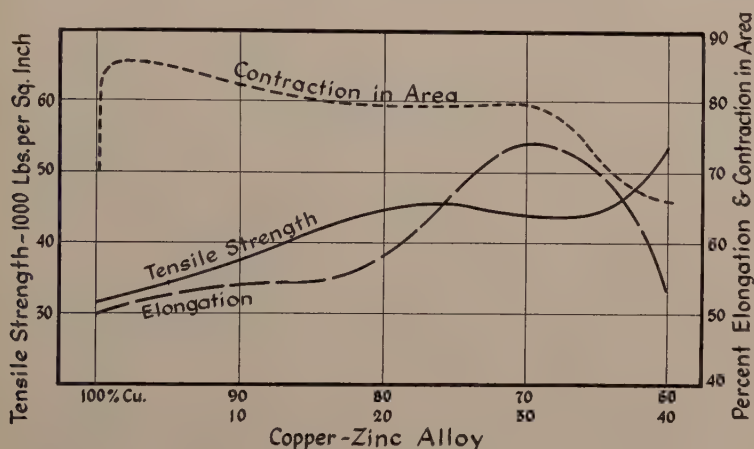


FIG. 1.—PHYSICAL PROPERTIES OF COPPER-ZINC SERIES, ANNEALED.

nonferrous alloys, because of their high resistance to ordinary corrosive agencies and the very wide range of properties that may be imparted to them by variations in the proportions of the constituents and by variations in mechanical treatment and heat-treatment.

Fig. 1 shows the normal physical properties, as determined by standard tensile tests, of the series when in the annealed condition. Fig. 2 shows the effect of varying amounts of cold-working on an almost pure

fied by the degree of cold-working to which a brass has been subjected, as shown by Fig. 4.

A fourth test, which is empirical, has been found useful because of its simplicity—the hot hammer test. Samples $\frac{1}{2}$ in. in diameter and $\frac{3}{4}$ in. long are placed in a suitable furnace. These are withdrawn one at a time at successively higher temperatures and are subjected to the blow of a drop hammer weighing 50 lb. with a drop of 4 ft. The percentages of reduction in length of the cylinders are plotted against temperatures and give a comparative measure of plasticity at different temperatures. The results of this test on several

* Chairman of the Board, Bridgeport Brass Co., Bridgeport, Conn.

† Presented at the New York Meeting, February 1942. Twenty-first Annual Lecture. Manuscript received at the office of the Institute Jan. 3, 1942. Issued as T.P. 1477 in METALS TECHNOLOGY, June 1942.

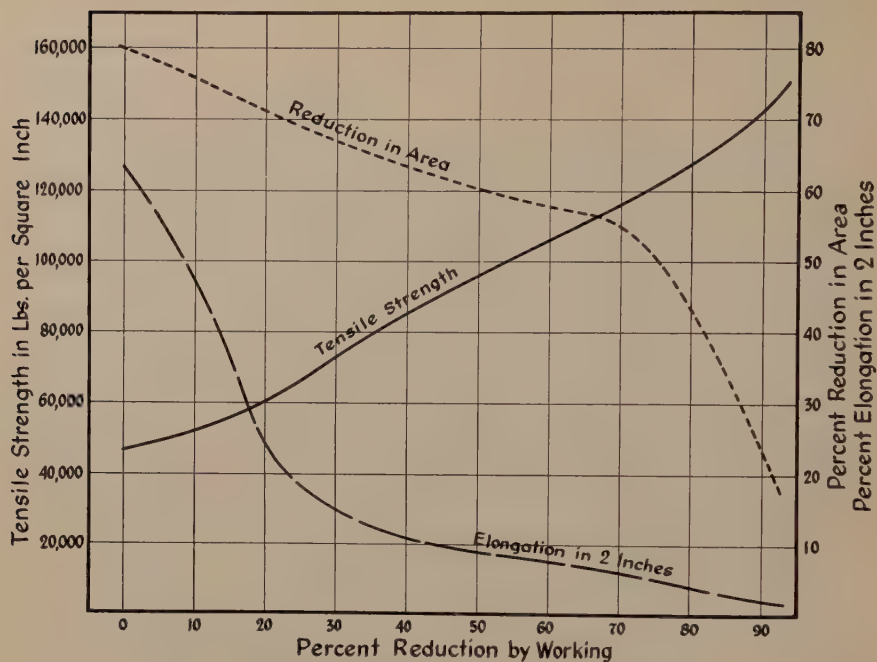


FIG. 2.—EFFECT OF VARYING AMOUNTS OF COLD-WORKING.

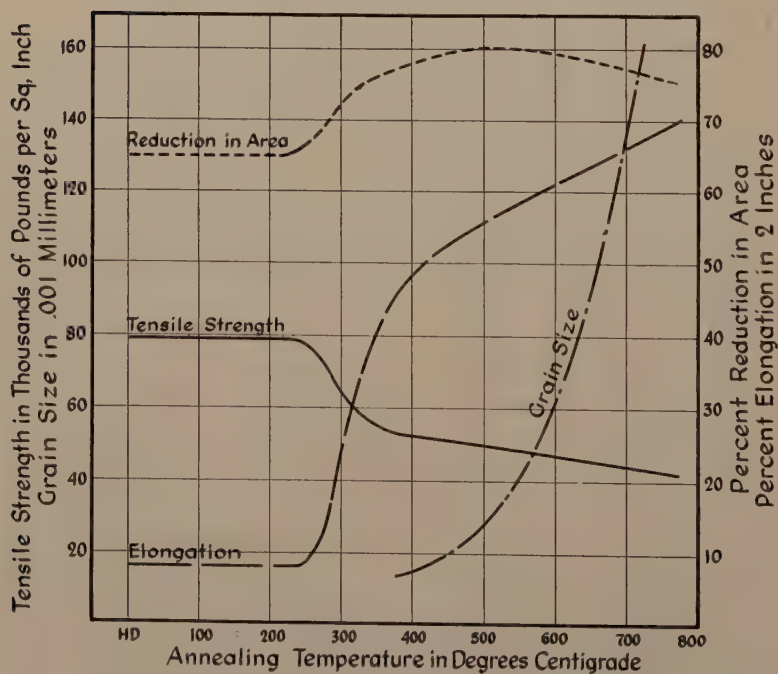


FIG. 3.—EFFECT OF ANNEALING AT VARIOUS TEMPERATURES.

mixtures are shown by Fig. 5. The broken line is a leaded brass of approximately 60 per cent copper and 3 per cent lead, which

perature—indicates the temperature at which edge cracking begins and to a degree the extent of it. This cracking indicates that

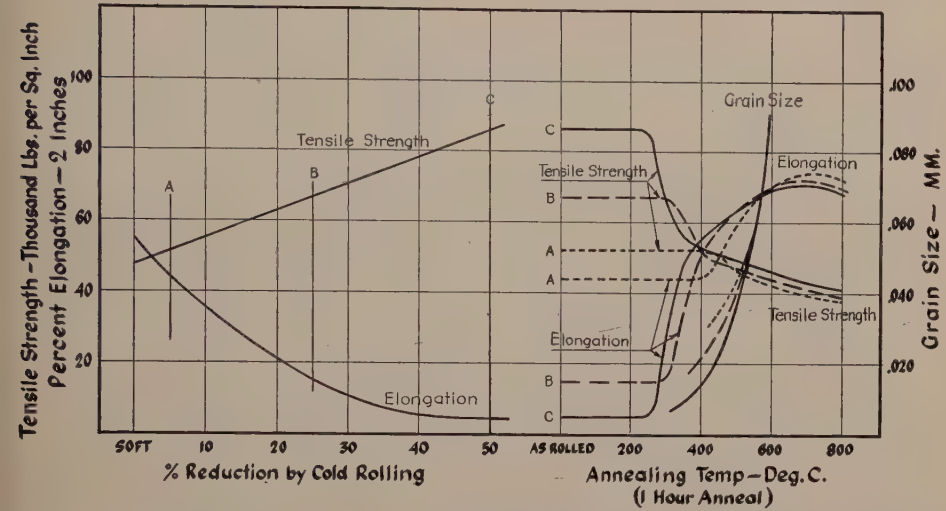


FIG. 4.—EFFECT OF AMOUNT OF COLD-ROLLING ON ANNEALING CHARACTERISTICS OF SHEET CARTRIDGE BRASS.

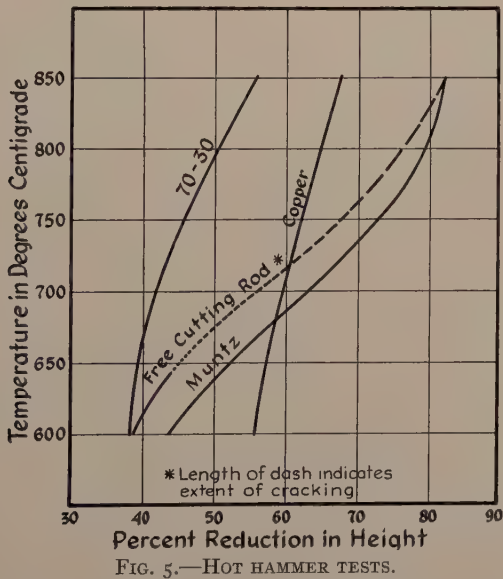


FIG. 5.—HOT HAMMER TESTS.

is the standard free-cutting brass for screw-machine purposes. The portion of this curve shown as a broken line—the dashes increasing in length with increase of tem-

this mixture cannot be successfully hot-rolled. It can, however, be readily extruded because with this process the particles of the hot metal are at all times in compres-

sion and not in tension. More accurate results can be obtained by means of hot tensile tests carried on at successively higher temperatures, but as these are somewhat troublesome and time-consuming the hot hammer test is usually an acceptable

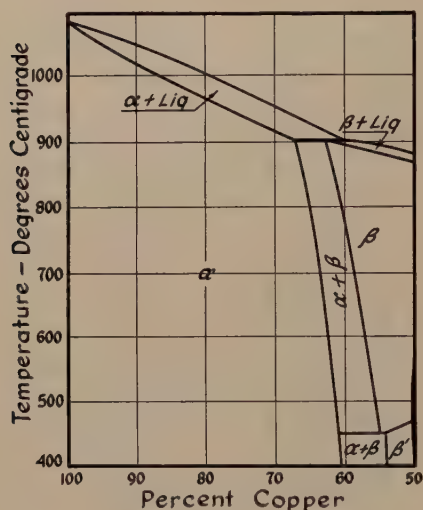


FIG. 6.—CONSTITUTION OF COPPER-ZINC ALLOYS.

substitute. All the brass alloys are readily formed by pressing operations and are easily machined. Their properties can be further modified by the addition of other constituents.

Of the metals usually added, lead is the most widely employed, as it greatly increases the cutting speed at which brass can be machined. The copper available is about 99.9 per cent pure, the major impurity being oxygen, which amounts to from 0.03 to 0.05 per cent. Zinc comes in several grades, depending upon the amount of lead it contains; this varies from 1 per cent or more to as little as 0.002 per cent. Lead has two effects; it favorably influences machinability and over most of the range it produces hot shortness and decreases cold-workability. This hot shortness varies somewhat with the copper content; between 57 and 62 per cent, 1 per cent or more

is not troublesome. Tin is added sometimes to improve resistance to corrosion and to increase strength and elastic properties. Over most of the range, brass contains a single alpha constituent, but from 57 to 62 per cent a second constituent, beta, appears. This is shown by the simplified constitutional diagram of the copper-zinc series, Fig. 6.

EARLY PRODUCTION OF BRASS

The origin of brass is lost in the mists of antiquity. The name appears frequently in translations of biblical and other ancient literatures, but undoubtedly bronze, an alloy of copper and tin, is meant, as that material was abundant centuries before brass was known. This confusion of terms still occurs; for instance, bronze field pieces frequently are called brass cannon.

Because of the relatively low temperature at which it melts, brass is employed for castings, large and small, but it finds its widest range of usefulness in the wrought state, and to its properties, uses and manufacture in this state this discussion will be hereafter confined.

The first authentic reference in literature to brass as distinct from bronze is by Dioscorides, in the first century, although this by no means determines the period when it was first employed.

Theophilus in the twelfth century described its manufacture by the fusing of calamine and copper with charcoal in crucibles, a method universally employed until the latter part of the eighteenth century. A somewhat detailed description of the process was published by Ercker in 1672.¹ This contains illustrations of the crucible, the crucible tongs, the melting furnace and the mold. A more complete description was given by Galon² in 1764, but the process as disclosed by him does not differ materially from that described by Ercker a century earlier.

¹ References are at the end of the paper.

Fig. 7 is a reproduction of a view of the casting shop given by Galon, showing a tub *V* in which the constituent ingredients were mixed, the crucible furnaces *A*, *B* and

There is ample evidence that the production of brass sheet had been carried on extensively for centuries before this. This evidence is supplied by the many monu-

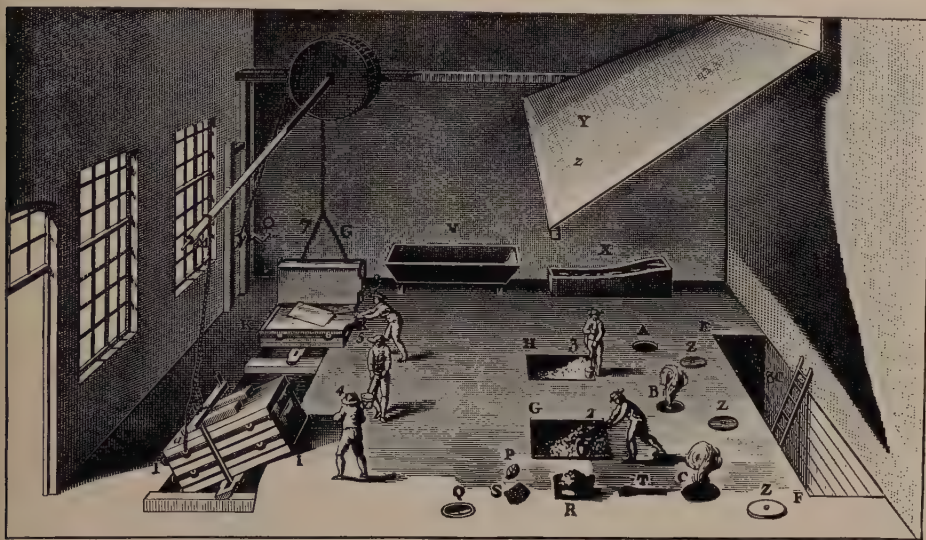


FIG. 7.—EIGHTEENTH-CENTURY CASTING SHOP.

Interior of foundry in County of Namur on the Meuse.

Illustration from paper by Galon before the Academie Royale des Sciences, 1764.

A, *B* and *C*. Openings to the furnaces in which the crucibles are heated.

E and *F*. Space from which the fires are tended.

G and *H*. Receptacles in which the crucibles are skimmed. These skimmings are afterward worked over to reclaim valuable metal.

I, *K* and *L*. Molds made of stone held together by iron frames.

N and *O*. Parts of the hoisting equipment for handling the molds.

R. Tub used for measuring calamine.

S. Represents small pieces of copper about 1-inch cube.

T. Paddle used for mixing and handling calamine.

V. Tub in which calamine and pulverized charcoal are mixed.

X. Bed, of which there are three in each foundry. The foundrymen stay on the job 24 hours for five days in the week.

Y. Apron for catching gases from skimming pits and furnaces and leading them to chimney flue.

Z. Covers to melting furnace.

C, the casters 2 and 3 skimming the dross from the top of the crucibles, a closed mold *I* in which the molten metal is poured and at *K* another mold, from which the casting is being withdrawn. As the melting and casting was at that time a continuous process, a couch *X* was provided for the repose of the caster between heats. After the metal was cast, the bars were reduced in thickness by tilt hammers run by a water wheel (Fig. 8).

mental brasses found in religious structures, particularly in England, which date back to the thirteenth century. Of these, 3000 or 4000 still exist, and it is thought that many more thousands were destroyed, particularly as their highest development occurred in the fourteenth century. It is interesting to note in passing that one made about the beginning of the sixteenth century was composed of 64 per cent copper, 29.5 per cent zinc, 3.5 per cent lead and 3 per cent

tin, a mixture that has not yet been surpassed for the purpose.

Wire was produced by shearing rectangular strips from a hammered bar or

BRASS INDUSTRY IN UNITED STATES

By the time that the use of calamine was abandoned the practice of the art had been

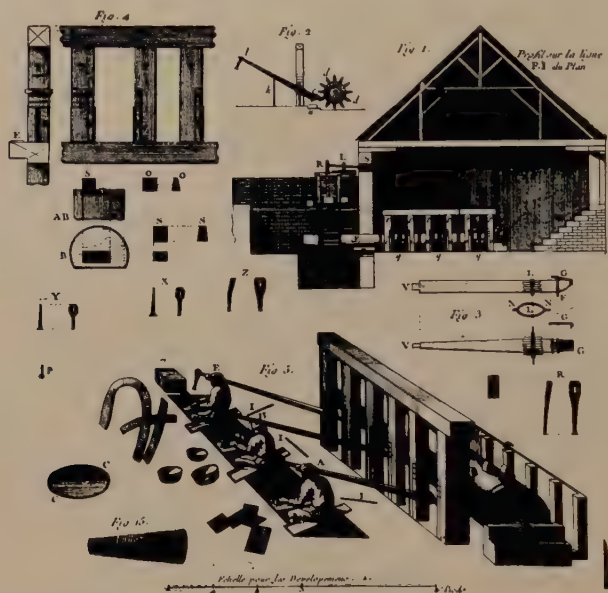


FIG. 8.—HAMMER SHOP OPERATED BY WATER POWER.

Details of brass-forging plant as shown in Fig. 7. Each water wheel operates a gang of three hammers. The cast bars and other shapes are worked into final form under the hammer. The descriptions that accompany these illustrations in the original manuscript tell how the metal is heated and annealed between the successive reductions under the hammer.

plate and then drawing them through dies on a vertical revolving block. Just when rolls instead of hammers were employed to reduce the thickness of the castings is not clear, but a work published in 1734 by Swedenborg describes a set of rolls driven by a water wheel through a gear train and pinion stand, for rolling brass and copper.

A major improvement in the art was accomplished in the latter part of the eighteenth century when metallic zinc was substituted for calamine. This probably permitted the use of a larger melting unit than had ever been employed and greatly hastened the time of melting. No material improvement in the casting process occurred until the introduction of electric melting, in the second decade of the present century.

well developed in England. In this country the industry began at Waterbury, Conn., about the beginning of the nineteenth century. At that time the inhabitants of Connecticut were engaged in many household industries, one of them being the manufacture of pewter buttons, which was extensively carried on in Waterbury. This did not require much equipment or very elaborate technique. The pewter was melted in the kitchen fireplace and the various operations involved were performed by members of the household. However, at this time Dame Fashion decreed that brass buttons were to be worn instead of pewter. The buttonmakers came of a hardy, resourceful and undaunted race. Their only salvation was to make brass buttons and brass and this they proceeded to do. The

art of sand casting was at that time understood and practiced in the locality. Accordingly bars of suitable dimensions were cast, taken to an adjoining community that possessed an iron rolling mill and there were partly rolled down. They were carried back to Waterbury and finish-rolled to the proper size on a small pair of rolls 2 in. in diameter, driven by horsepower. That was the beginning of the industry, in the development and growth of which Waterbury and its vicinity have played a major part. Many problems had to be solved, and not until some years later, when equipment and skilled labor were brought from England, under great difficulties, did the industry become firmly established. Tradition has it that in order to avoid legal complications skilled workers were in one instance packed in wine casks in order to get them out of England.

Up to about 1830 the business was one of small beginnings and small accomplishments, being confined to two establishments in Waterbury, and the production was confined to sheet brass. In 1830, however, when a third establishment was formed one of its executives went to England and returned with a complete equipment of the latest machinery and a force of skilled workmen. In addition to the rolling of sheet, this establishment produced wire and brazed tubing, the latter product then coming into extensive use for the manufacture of gas fixtures.

The vicinity of Waterbury had for a considerable period been the home of the clock industry. This had employed wood for the mechanism, but when it was found that brass was much better for this purpose the demand for the metal increased and a much larger output became necessary. About the same time, machinery for making pins was invented, which consumed large quantities of brass wire. However, the total output of all of the mills at that time scarcely exceeded a ton a week. Much difficulty was experienced in obtaining the

necessary raw materials. At first scrap articles of various kinds, made of both copper and zinc, were used. In 1850 a company of Waterbury men organized and built a smelter in which to handle Michigan copper, the deposits of which had recently been discovered. At the close of the Civil War, zinc smelting was undertaken in Missouri, and provided an ample supply of this material.

The Naugatuck Valley, in which Waterbury is situated, was a particularly favorable place for the initiation and growth of the industry, as it furnished easily developed water power and wood for annealing purposes. The Naugatuck River from Torrington, where it is formed by the confluence of two branches, to Derby, where it enters the Housatonic, is 32 miles long and has a fall of 600 ft. in that distance. Fifteen dams have been built across it. In addition, it has numerous tributaries, which also supply power. In 1884 there were eight different concerns at Waterbury, which had a combined output estimated at 75 per cent of the entire industry of the United States. At the present time, Connecticut companies and branches outside of the state controlled by Connecticut companies still produce about the same proportion of the total.

It is unlikely that an industry concerned with a product that is in such universal demand can be confined to one small locality, and about 1884 several concerns outside the state were organized. At the present time there are about 30 establishments throughout the East and Middle West that produce brass in various forms. The first product was sheet brass but rods, wire and brazed tubing were added as the demands of the market required. An English patented process for making seamless tube was employed by a company near Boston about the middle of the century and considerably later other companies undertook the manufacture of the same product.

METHODS

While English methods were closely followed from the beginning, some im-



FIG. 9.—PIT-FIRED CASTING SHOP.

provements were developed here, until at the end of the century practice was well standardized. The metal was melted in graphite crucibles holding about 200 lb., which were heated in pit fires burning anthracite. These fires were arranged in long rows connected to an ample stack and were handled in sets of eight or ten, each group being operated by one caster and two helpers. After being melted and heated to the proper degree, the metal was poured into banded cast-iron molds producing bars of various widths and lengths, usually about $1\frac{1}{8}$ in. thick. Fig. 9 shows a casting shop with the melting furnaces in the back-ground and Fig. 10 a caster pouring the contents of a pot or crucible into a mold.

Until toward the end of the century, wire and rods of small diameter were made by gang-slitting a flat-rolled bar into strips, which were drawn to the required size on

wire blocks. Large rods were made from round castings or bolts drawn to size on chain-driven drawbenches. Both processes were later superseded by rolling a bolt cast-



FIG. 10.—CRUCIBLE CASTING.

ing in grooved rolls, the finishing operations employing wire blocks and drawbenches as before.

In the manufacture of sheet several stands of rolls employing chilled cast-iron rolls were driven through gearing from a common shaft. Three steps were employed: breaking down (involving several passes through the rolls) carried the bar to about $\frac{5}{8}$ in. thick; running down similarly carried it to about $\frac{1}{16}$ in. thick, then it was transferred to the finishing rolls, where it was reduced to the required finished thickness. The breaking down rolls were usually 18 to 20-in. diameter by 30 to 36-in. face, with 18-in., 16-in. and some smaller stands for running down and finishing. For exceptional sizes of sheets, larger rolls were employed. After about 50 per cent reduction, the metal became too hard for further rolling. It was then annealed on iron pans in open-

fired flat-hearth furnaces. In the early years of the industry wood usually was the fuel, and was particularly well adapted for this use, but later the failure of the supply of wood necessitated the substitution of coal and oil.

After the breaking-down rolling, the surfaces of the bars were machined or "scalped" by a reciprocating tool mounted in a machine that permitted all parts of the surface of the bar to be successively presented to the action of the tool. By a simple arrangement the amount of metal removed at any point could be varied according to the depth of surface defects encountered. In later years a slab-type milling machine took the place of this. Before being sent to the finishing rolls the metal was immersed in a weak sulphuric acid bath or pickle, after which it was thoroughly washed with water. Because of the latter operation, it was desirable that the mills be near an ample water supply, as they always were as long as they were driven by water power. Fig. 11 shows the usual type of finishing mill.

Finish rolling left the metal with varying degrees of hardness, dependent on the amount of reduction necessary for any specific use. Similarly, it might be annealed to varying temperatures, according to the purpose for which it was to be employed. After the final anneal, it was pickled and washed and the surface was dried mechanically, to prevent staining. Finally, it was slit or sheared to required dimensions and shipped either in coils or flat lengths.

As the volume of business increased, endeavors to meet it were made all along the line. Certain difficulties were experienced as heavier bar castings were employed. As thicknesses decreased, lengths became difficult to handle. On emerging from the rolls, the strips at first were formed in coils by hand, but in 1886 a three-roll coiler was invented, which formed the metal into coils automatically as it came from the rolls and not only speeded

up production but saved labor. Another limitation to increased roll speeds arose from the difficulty of coiling metal thinner than could be handled by the three-roll

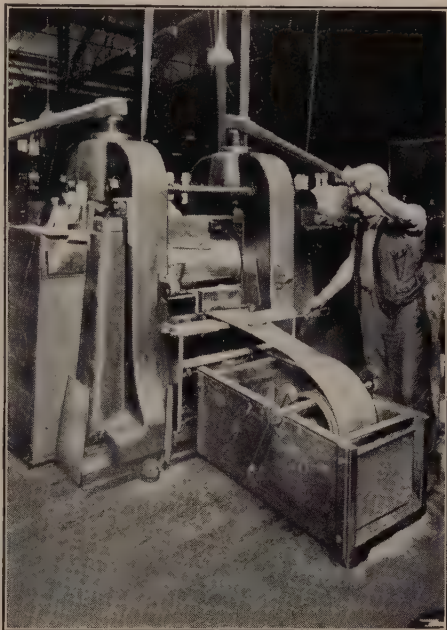


FIG. 11.—SHEET-FINISHING MILL.

coiler. As the strip left the rolls, it was manually engaged with a horizontal revolving drum known as a block. This was at all times a hazardous operation because the fingers of the worker might be caught between the strip and the block and cause serious injury. Moreover, it was impossible to perform the operation at all at speeds higher than about 200 ft. per minute. This difficulty was obviated by the invention of the automatic blocker, in 1905. This eliminated hand labor and permitted finishing speeds up to 750 ft. per minute, or more.

ELECTRIC MELTING

It became apparent that further progress must await the development of a melting unit that would provide a larger casting than could be satisfactorily furnished by

the crucible. This came in 1916, when the industry was revolutionized by the introduction of the low-frequency electric melting furnace which, following the war,

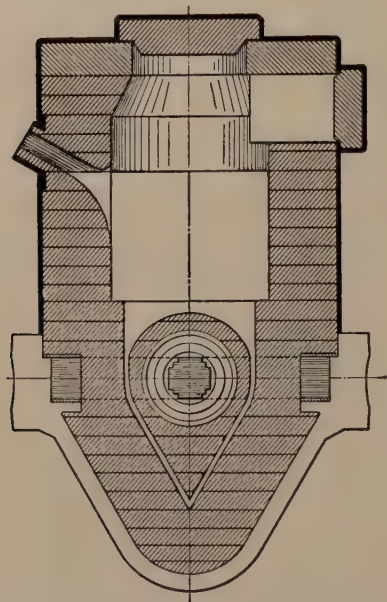


FIG. 12.—LOW-FREQUENCY ELECTRIC MELTING FURNACE.

rapidly came into universal use. In effect, this furnace consists of a transformer of which the secondary is a refractory channel filled with molten metal when the furnace is in operation, which is joined with the main body of the furnace to form a complete electric circuit. Before the furnace can be started it must be partly filled with molten metal from an existing source. Current flowing through the primary circuit induces a current in the secondary of sufficient intensity to raise the temperature of the metal comprising it. At the same time, a vigorous circulation, due to electrical forces, is set up in the channel enclosing the secondary, which ejects the superheated metal therefrom into the main body of the furnace, thereby melting cold metal as it is charged into the latter. Fig. 12 shows the furnace diagrammatically.

As this process passed the experimental stage, which it did rapidly, larger sizes of furnaces were built (Fig. 13). Some of the new mills being constructed under the armament program will employ furnaces of 200 to 250 kw., capable of making castings weighing about 2000 lb. Few improvements of such a revolutionary character have ever come into universal use so rapidly, particularly as the patents covering it have not yet expired. It is a safe estimate that over 90 per cent of all brass made by wrought processes all over the world is melted in these furnaces.

As previously stated, small sizes of rods were made originally by slitting and drawing on wire blocks and larger sizes by drawing from a round casting or bolt, later refinements involving the use of grooved rolls for initial reductions.

HOT EXTRUSION

A method of hot extrusion was invented and patented in England and shortly thereafter a machine was brought to this country (about 1896). For some years this method had a restricted use, its product being mainly employed for architectural moldings. Because of the limitations of the steels available, it could be used only on mixtures of high zinc content, whose mechanical properties limited its use to a very large degree. With the expiration of the patent and the invention of high-speed steel late in the first decade of the present century, this process was able to handle the entire range of the copper-zinc alloys as well as more refractory ones. The development of the automatic screw machine called for very large quantities of highly leaded brass rod, for the production of which this process was particularly well adapted.

In passing it may be noted that this furnishes an example in a particular instance of the dependence of progress in one art upon that in another. Prior to the invention of the high-speed steels the use-

fulness of the extrusion machine was exceedingly limited. With their appearance it became one of the most useful of tools employed in the brass industry and is now

finishing draft on a block or drawbench. It has not usually been practicable to extrude smaller than about $\frac{1}{2}$ in. Reduction to smaller sizes for rods or wire requires



FIG. 13.—ELECTRIC MELTING FURNACE AND MOLD.

responsible for 30 per cent or more of all brass production. With the slitting process the weight of coils of brass wire was limited to about 12 or 15 lb. and with rolled rods to about 60 lb., but when made by the extrusion process coils of about 250 lb. became available. At the same time the quality of the product was much improved.

The extrusion machine consists of a horizontally arranged hydraulic press, one portion of which is a heavy walled cylinder or "container" closed at one end by a die. The plunger of the hydraulic press reciprocates within this container a loose-fitting plunger. In action a heated billet is inserted within the container, after which the plunger forces the metal of the billet through the die in the form of a rod, which may have any desired contour. The extruded rod, after pickling, is given a

drawing on a wire block, and for rods straightening on a machine designed for that purpose. The machines heretofore have had a capacity of 1500 to 2000 tons, but several are now building up to 4000 tons. With the first mentioned capacities billets ranged from 6 to 8 in. in diameter, weighing from 200 to 350 lb. With the larger machines now building, 800-lb. billets will be used. When it is realized that these are reduced to $\frac{1}{2}$ -in. diameter in about one minute the value of the process will be understood.

SEAMLESS TUBES AND SHEETS

As mentioned, the manufacture of seamless tubes was introduced from England about the middle of the century, but it was not undertaken by the other mills for about 25 years thereafter. Standard practice comprised the casting of a hollow

shell using a sand core, similar in construction to that used in the manufacture of cast-iron pipe, inserted in a vertically positioned cast-iron mold between which

World War, this process was employed by other mills, with a corresponding reduction in the employment of the shell process. Also before the World War, the



FIG. 14.—TUBE-EXTRUSION MACHINE.

and the sand core the metal was poured. After casting, the shell was placed on a steel mandrel, which pulled or pushed it through a reducing die for several operations, wherein both the diameter and wall thickness were successively decreased and the length was increased. The tube was reduced to successively smaller diameters and thicknesses by cold-drawing, by means of a drawbench through a die and over a plug or triplet held in position in the die by a stationary rod that carried the plug.

In 1894 one of the mills at Waterbury procured the American rights for the Mannesmann piercing process, invented in Germany. Although entirely successful in connection with the manufacture of copper tubes, its use was confined to a single brass mixture that could be worked hot. It is interesting in this connection to note that the use of this process antedated the introduction of the piercing process in this country in connection with the manufacture of steel tubes. Shortly before the

use of the extrusion process for making seamless tubes was successfully developed abroad but because more exacting specifications were required in this country it was not sufficiently perfected for use here until some years later. About 10 years ago the process was introduced into this country and is now in general use. It is not as economical as the piercing process for mixtures that can be readily pierced, but it handles successfully a number of important mixtures that cannot be pierced. In order to make tubes the rod machine is modified by the addition of a second pressure cylinder carrying a piercing mandrel having a diameter equal to the required inside diameter of the tube. After the billet is placed in the container the piercing mandrel is advanced until the billet is completely pierced, then the mandrel and extrusion plunger travel together until the operation is completed. Fig. 14 shows a recently installed machine of this type. Because of the small volume

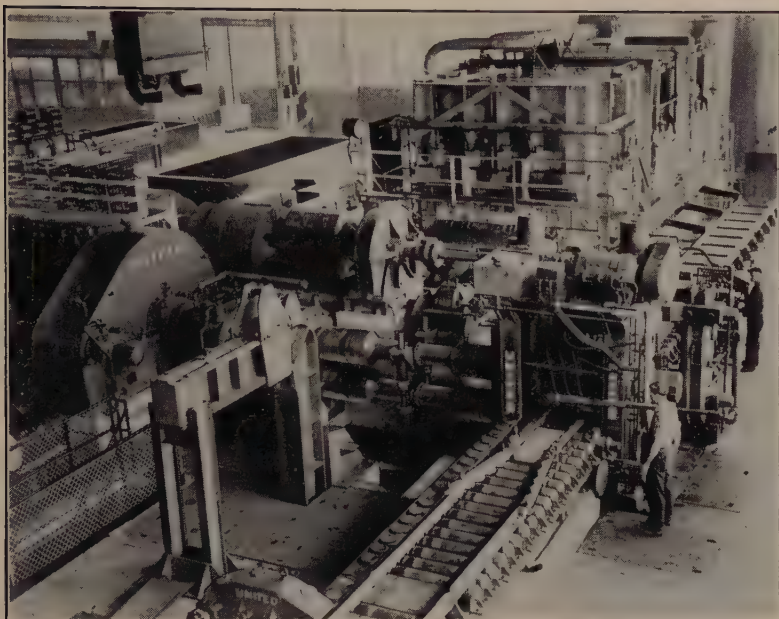


FIG. 15.—MODERN HOT BREAKING-DOWN MILL.

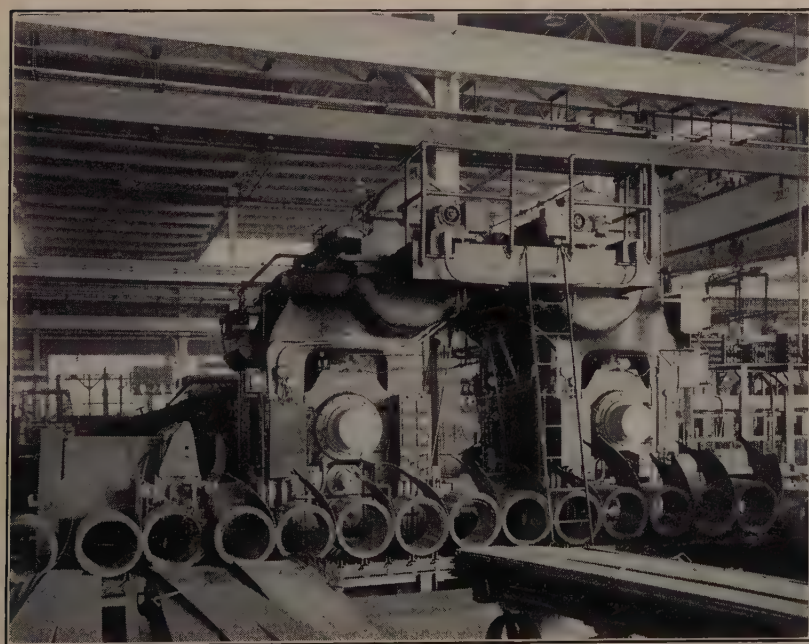


FIG. 16.—MODERN TANDEM FOUR-HIGH RUNNING-DOWN MILL.

required, large sizes are still made by piercing or by the cast shell process, both in brass and in copper.

The introduction of the electric furnace, with the larger melting unit and closer control of temperatures and mixtures it made possible, not only materially improved the quality of both rods and tubes—it revolutionized the brass sheet mill. The latest practice employs bar castings weighing from 600 to 1000 lb. These necessitate much heavier rolling equipment and mechanical handling methods throughout. For cold breaking down, rolls 26 in. in diameter by 36 in. long, completely equipped with mechanical handling devices actuated by push button and hand-lever control, are employed. The large quantities of brass required for small arms and artillery cartridge cases, as well as other mixtures that are capable of being worked hot, permits hot breaking down, as a consequence of which a reversing universal breaking-down mill closely following those used in steel mills represents the latest practice. Running down is done on four-high mills in tandem. Finishing is done on four-high and two-high mills, according to requirements, most of the handling being done mechanically (Figs. 15 and 16). Overhauling, after breaking down, is done on a heavy slab miller. With these have come important improvements in annealing and pickling facilities as well as in methods of handling from operation to operation.

CONTINUOUS CASTING

For many years inventors have been intrigued by the possibility of continuously casting metal by pouring it into a confining channel within which it would be caused to solidify and from which it would be drawn in a continuous length. Many patents have been issued covering devices for this purpose, some of which have been experimentally successful and two at least commercially so. One of the latter devel-

oped in Europe has been in use here for several years. By this method, molten metal is poured continuously into the upper end of a vertical tubular mold surrounded by a water jacket. The metal solidifies in this mold and is drawn continuously therefrom in a solid bar by pinch rolls. A saw traveling with the casting cuts it into appropriate lengths. This machine, as far as its use in this country is concerned, has been confined to casting round billets for the extrusion process, but under the armament program will be used for the casting of sheet bars also. The process is as revolutionary in its nature as was that of the electric furnace. It is destined to come into extensive use in one form or another. Some success also has been achieved experimentally in continuously rolling sheet or strip from molten metal. Ultimately this may importantly affect the methods of making sheet and strip.

CONTROL OF PROCESS

Until about 50 years ago, the operations of the industry were conducted almost exclusively by rule of thumb. Experience was the sole guide. It was well understood that if certain procedure was followed a satisfactory product would follow. Generally but three measurements were involved, the weighing of the components of the crucible charge, the measurement of the dimensions of the material as finished and the shipping weight. In spite of these limitations, however, the quality of the material was high even by present standards. Probably this was because the processes employed in the further fabrication of the material themselves constituted efficient tests of quality. If it failed to pass such tests the producer well knew that he could expect to have it returned, and that he had no tests of his own by which to refute a customer's contention. However, the use of the electric melting furnace and pyrometric temperature control have

resulted in a much greater degree of uniformity.

Practically all of those engaged in the operations of production had come up the hard way and through the school of experience. There was no dependable literature to assist them. Moreover, those possessing expert knowledge or skill looked upon it as a capital asset, which would be depleted by imparting it to others, hence much mystery.

Gradually, however, large users began to write specifications, which demanded the making of chemical analyses and physical tests. In this way technically educated people were brought into the industry and began to make themselves felt. Research departments were organized

and developed until at the present time every step or process from metal room to shipping is under accurate control. The number and quality of papers presented before this and other societies amply testify to the high character of work done by these organizations in recent years.

The defense program has placed a heavy burden on the brass industry but it presents no new problems. It may be expected to do its full part.

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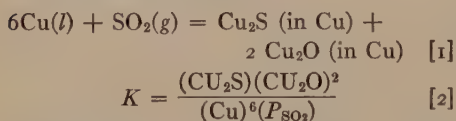
1. L. Ercker: *Untererdische Hofhaltung*. Franckfurt am Mayn. J. D. Junger Buchhandlers. 1672.
2. M. Galon: *L'art de convertir le cuivre rouge ou cuivre de rosette en laiton ou cuivre jaune*. *Proc. Acad. des Sciences, Inst de France* (1764) 5.

Effect of Impurities on the Solubility of Sulphur Dioxide in Molten Copper

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(New York Meeting, February 1942)

A YEAR ago the authors published a paper on the solubility of sulphur dioxide in molten copper.¹ The data in that paper agreed closely with that obtained by previous investigators, which, however, did not agree with the theoretical predictions for solubility of triatomic gases of this type. It has generally been assumed that the reaction of solution is:



Neglecting the slight change in copper concentration and considering that the concentrations of sulphur and oxygen are both proportional to the volume of gas absorbed, it follows that this volume should be proportional to the cube root of the pressure. It was found that a plot of the volume absorbed versus the cube root of the pressure gave a straight line, but that this line did not pass through the origin. Calculations of the equilibrium constant for the reaction showed that it was fairly constant for pressures above 100 mm. but that actually it approached zero at lower pressures. The conclusion was made therefore that the solubility as determined could not be expressed by Eq. 1 or by any other simple equation, particularly at low pressures.

Other investigators have concluded that the solubility of sulphur dioxide in copper

as well as in several copper alloys is more nearly proportional to the square root of the pressure.* Such a conclusion, however, does not satisfactorily account for the results, even when rather complicated mechanisms for the solution are assumed. The highly improbable speculations of Lepp² and of Schneider and Esch³ based upon hypothetical dissociation pressures of Cu_2O and Cu_2S dissolved in copper illustrate the type of reasoning that has been used to account for the discrepancy.

In the discussion of the previous paper, the authors pointed out that the discrepancy might possibly be due to impurities in the copper, although the purest form available was used. Further consideration of the problem suggested that the impurities likely to have the greatest effect on the solubility of SO_2 in copper were oxygen, sulphur and carbon. Accordingly, further experiments have been made to show the effects of these elements.

EXPERIMENTAL METHODS

The apparatus used for measuring solubility was essentially the same as that shown in the previous paper. However, since it was desired to make measurements at low pressures, a McLeod gauge was added and 6-mm. glass tubing was substituted for the capillary. This increased the "hot volume" considerably but was necessary in order to obtain good vacuums in a reasonable length of time. A mercury diffusion pump was also installed.

Manuscript received at the office of the Institute Dec. 1, 1941. Issued as T.P. 1435 in METALS TECHNOLOGY, February 1942.

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¹ References are at end of paper.

* See references at end of previous paper.¹

As in the previous work, OFHC brand copper of commercial purity was used for all runs. Since copper ordinarily is deoxidized with carbonaceous materials, carbon is very likely to be present. Leonard⁴ has shown that the solubility of carbon in copper is not insignificant and may be as high as 0.003 per cent. The effect of an impurity of this kind on the solubility of SO_2 will be an indirect rather than a direct one, resulting from the experimental method used for measuring solubility; that is, any carbon present in the copper will react with the SO_2 , forming CO or CO_2 and thus increasing the pressure in the system. In an apparatus of the type used the pressure readings therefore will be higher than the actual partial pressure of the SO_2 , the magnitude of the error being proportional to the amount of CO or CO_2 evolved. The quantity of carbon necessary to produce considerable error is small, as is shown by the fact that 0.001 per cent of carbon in 100 grams of copper will form 2 c.c. of CO , which, if the hot volume of the system is 30 c.c., will cause a partial pressure of about 50 millimeters.

Purification of Copper.—The elimination of carbon from the copper before the beginning of the solubility determinations, therefore, becomes very important. This was done by adding 0.5 grams of Cu_2O to each 100 grams of copper charge, which is more than sufficient to oxidize all of the carbon. After melting in vacuum, the system was pumped out for approximately 2 hr. to a pressure of about 0.003 mm. The elimination of carbon from the molten metal is very slow, as witnessed by the fact that so long a pumping time was necessary.

The excess of oxygen was next removed by treatment with hydrogen for approximately 2 hr. Successive additions of hydrogen were made until no further condensation of water could be observed in the cold parts of the system. The melt was then held in dry hydrogen for about 30 minutes.

Next, the system was again evacuated for about 2 hr. From the results obtained, it appears that this treatment did remove nearly all of the carbon, although, as will be shown later, prolonged pumping apparently would be necessary to eliminate the last traces. During the melting of the copper in the presence of Cu_2O , a pressure of about 15 mm. was built up in the system. Assuming that this was due to the formation of CO , it may be calculated that the amount of carbon removed during melting was of the order of 0.0004 per cent. However, the length of time required to obtain a vacuum after melting indicates that the removal of the last trace of carbon is very slow. Therefore, the indications are that the original copper actually contained more carbon than is indicated by the pressure developed during melting, and that the purified copper may have retained a trace of carbon even after the prolonged treatment. There is also a possibility that traces of carbon were reintroduced into the metal during the hydrogen treatment by small amounts of hydrocarbons in the hydrogen.

Experiments with Excess Sulphur.—In the experiments in which an excess of sulphur was used, cuprous sulphide was added to the charge after the hydrogen treatment. It was added in vacuum from a special tube fastened by means of a ground joint to the upper part of the fused silica vessel in which the copper was melted. After treatment with hydrogen and pumping to vacuum this tube was turned in such a way as to allow the Cu_2S to fall into the molten copper.

The cuprous sulphide was prepared free from carbon by heating electrolytic copper powder with sulphur in Pyrex tubes and finally melting in fused silica, both operations being carried out in vacuum.

Experiments with Excess Oxygen.—To obtain a high initial concentration of oxygen, measured amounts of oxygen gas were added to the molten copper. In this case no

copper oxide was added in the charge and the hydrogen treatment was eliminated.

When the oxygen concentration of the molten copper is high, there is always danger of reaction between the Cu_2O and the fused silica crucible. To prevent this as much as possible the run was first made at 1100°C . only. A few high-pressure points were then determined at 1200°C ., but these were somewhat erratic, partly because of crucible reaction and partly because the measurements were made as rapidly as possible to minimize the amount of Cu_2O leaving the metal. After solidification, the amount of oxygen in the copper was determined by the vacuum-fusion method.

RESULTS OF EXPERIMENTAL WORK

Solubility of SO_2 in Pure Copper.—The solubility of SO_2 in pure copper at 1100°C ., 1200°C . and 1300°C . as a function of the pressure is shown in Table 1 and graphically

TABLE 1.—*Solubility of Sulphur Dioxide in Molten Copper*

Temperature, Deg. C.	Equilibrium Pressure, Mm. Hg	SO_2 Absorbed per 100 Grams Cu, C.C.	Sulphur or Oxygen, Per Cent	$\frac{\%S \times \%O_2}{P_{\text{SO}_2}}$
1100	4.18	24.7	0.0353	1.05×10^{-5}
	12.29	35.6	0.0508	1.07
	54.3	59.2	0.0845	1.11
	137	81.0	0.1170	1.17
	394	117.9	0.1685	1.22
	680	145.8	0.2081	1.32
1200	0.61	12.36	0.0177	0.91
	1.53	25.2	0.0300	3.05
	6.89	36.7	0.0524	2.09
	29.2	61.1	0.0872	2.27
	77.5	86.4	0.1234	2.42
	240	130.1	0.1856	2.67
	477	163.4	0.2332	2.66
	615	178.0	0.2541	2.68
	704	195.0	0.2785	2.83
1300	4.0	37.3	0.0532	3.76
	45.5	88.8	0.1207	4.49
	323	176.1	0.2517	4.94
	542	214.0	0.3055	5.26
	669	234.0	0.3342	5.59

in Fig. 1. By comparison with the previous paper, the solubility at low pressures is much greater than was previously found, but at high pressures the agreement is fairly good. This is what would be expected

if the previous discrepancies are considered to be due to the presence of small amounts of carbon.

The temperature coefficient of solubility is high at all pressures. This is illustrated by Fig. 2, which shows the variation in solubility with temperature at constant pressure. The values for this graph have been scaled from Fig. 4, to which reference will be made

TABLE 2.—*Solubility of SO_2 in Molten Copper Containing an Excess of Oxygen*

Temperature, Deg. C.	Equilibrium Pressure, Mm. Hg	SO_2 Absorbed per 100 Grams Cu, C.C.	Sulphur, Per Cent	Oxygen, Per Cent	$\frac{\%S \times \%O_2}{P_{\text{SO}_2}}$
1100	191.5	13.95	0.0199	0.389	1.57×10^{-5}
	469	32.45	0.0464	0.415	1.70
	696	46.05	0.0665	0.436	1.82
	862	56.5	0.0806	0.450	1.89
1200	448	55.5	0.0792	0.378	2.53
	641	73.0	0.103	0.402	2.60
	795	85.6	0.122	0.421	2.72

later. In the range covered the solubility is a linear function of the temperature at all pressures.

Effect of Excess Oxygen.—The effect of an excess of oxygen on the solubility of SO_2 in copper at 1100°C . and 1200°C . is shown in Table 2 and graphically by the lower curves in Fig. 1. The amount of oxygen added was 0.36 per cent. For the calculations at 1200°C . this figure was corrected for the amount of oxygen leaving the melt by reaction with the crucible. The solidified ingot was analyzed for oxygen and found to contain 0.329 per cent. On the basis of the original quantity of oxygen added plus that dissolved from the gas and minus that evolved as gas during solidification, it was calculated that the quantity remaining in the ingot after solidification should have been 0.399 per cent. It was, therefore, assumed that 0.070 per cent oxygen was consumed by crucible reaction and, therefore, that the effective excess of oxygen at the beginning of the determinations at 1200°C . was 0.299 per cent. As would be

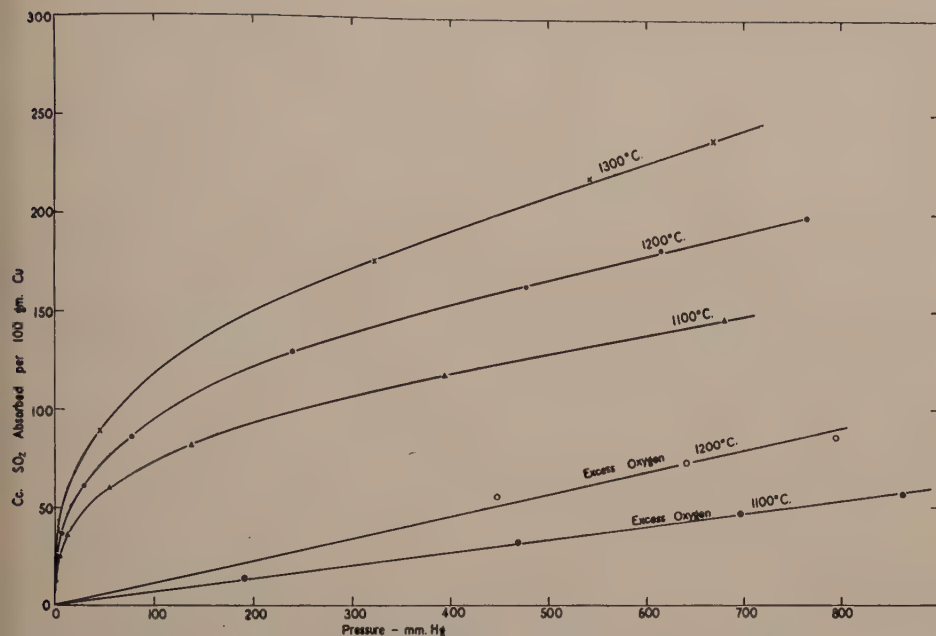


FIG. 1.—SOLUBILITY OF SULPHUR DIOXIDE IN PURE MOLTEN COPPER AS A FUNCTION OF PRESSURE. The two lower curves are for copper containing an excess of oxygen.

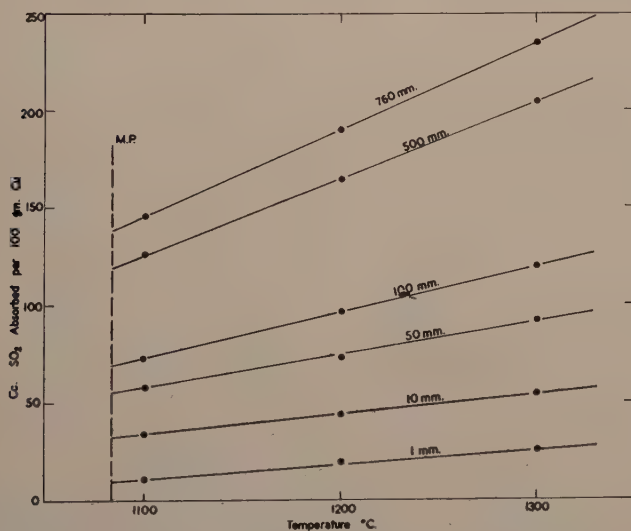


FIG. 2.—SOLUBILITY OF SULPHUR DIOXIDE IN PURE MOLTEN COPPER AS A FUNCTION OF TEMPERATURE.

expected, the presence of oxygen greatly decreases the amount of SO_2 absorbed.

Effect of Excess Sulphur.—The effect of an excess of sulphur on the solubility of SO_2 in copper is shown in Table 3 and graphically in Fig. 3. The amount of SO_2 dissolved is considerably decreased by the presence of the excess sulphur.

The amount of sulphur added was 0.387 per cent, determined as follows: Chemical analysis of the ingot showed 0.485 per cent sulphur. The gas evolved during cooling and solidification was 94.5 c.c., corresponding to 0.136 per cent sulphur. The liquid metal at the end of the run, therefore, contained 0.621 per cent sulphur, of which 0.234 per cent corresponds to the measured gas absorption of 163.8 c.c. at 1300°C .

TABLE 3.—*Solubility of SO_2 in Molten Copper Containing an Excess of Sulphur*

Temperature, Deg. C.	Equilibrium Pressure, Mm. Hg	SO_2 Absorbed per 100 Grams Cu, C.C.	Sulphur, Per Cent	Oxygen, Per Cent	$\%S \times \%O_2$ P_{SO_2}
1100	1.21	2.03	0.390	0.0029	0.33×10^{-5}
	10.78	11.61	0.404	0.0166	1.03
	67.0	30.1	0.430	0.0430	1.87
	158	46.5	0.453	0.0664	1.26
	379	73.7	0.492	0.1052	1.44
	590	91.3	0.517	0.1304	1.49
	863	103.6	0.535	0.1480	1.36
1200	1.00	2.08	0.390	0.0030	0.34
	2.45	5.89	0.395	0.0084	1.14
	6.82	12.49	0.405	0.0179	1.90
	41.5	32.5	0.433	0.0464	2.24
	99.5	52.0	0.461	0.0742	2.55
	267	84.2	0.507	0.1201	2.73
	435	107.1	0.540	0.1530	2.90
	650	126.2	0.567	0.1800	2.83
	834	144.5	0.593	0.2062	3.03
1300	1.66	6.07	0.396	0.0087	1.79
	4.44	13.02	0.406	0.0186	3.14
	67.2	54.8	0.465	0.0782	4.23
	309	119.3	0.557	0.1703	5.22
	486	142.7	0.591	0.2038	5.05
	645	163.8	0.621	0.2338	5.26

DISCUSSION OF RESULTS

Assuming that Eq. 1 is correct, the solubility of SO_2 in molten copper should be approximately proportional to the cube root of the pressure. A plot of the volume absorbed versus the cube root of the pres-

sure is shown in Fig. 4. The points for the three temperatures 1100° , 1200° and 1300°C . lie quite well on straight lines that pass through the origin. At very low pressures the points lie slightly below the lines, which is believed to be due to failure to eliminate the last traces of carbon. This would result in a small partial pressure of CO , which, however, might be sufficient to cause the slight deviation from the straight lines. These results should be compared to those previously published, where, because of failure to eliminate the carbon, the cube-root plot gave straight lines that intersected the pressure axis at considerable distances from the origin. For the present results, the agreement with the cube-root relationship is sufficiently close to prove that Eq. 1 essentially represents the reaction of solution.

When the initial concentration of oxygen in the copper is high, as in the data given in Table 2, the absorption of SO_2 causes only a small fractional increase in the Cu_2O term of Eq. 2. Therefore, regarding this term and the metal concentration as approximately constant, the volume of SO_2 absorbed becomes directly proportional to the pressure. That this is true is shown by the fact that the points for 1100°C ., plotted on the lower curve in Fig. 1, lie on a straight line passing through the origin. The points for 1200°C . deviate from this straight-line relationship, which, however, is experimental error as previously discussed.

Similarly, when the initial concentration of sulphur is high as in Table 3, the percentage change in the Cu_2S term in Eq. 2 is small enough to be neglected and the volume of SO_2 absorbed becomes proportional to the square root of the pressure. To check this a plot was made as shown in Fig. 5, in which the volume of gas absorbed has been plotted against the square root of the pressure. The points for each temperature do fall quite well on straight lines passing through the origin. Again, as with pure copper, the points at low pressures

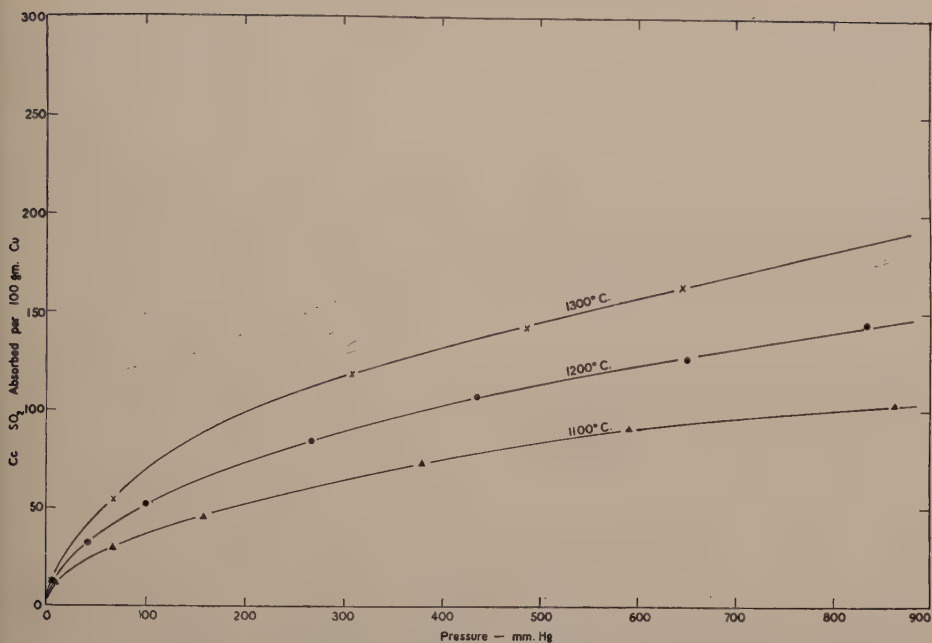


FIG. 3.—SOLUBILITY OF SULPHUR DIOXIDE IN MOLTEN COPPER CONTAINING AN EXCESS OF SULPHUR AS A FUNCTION OF PRESSURE.

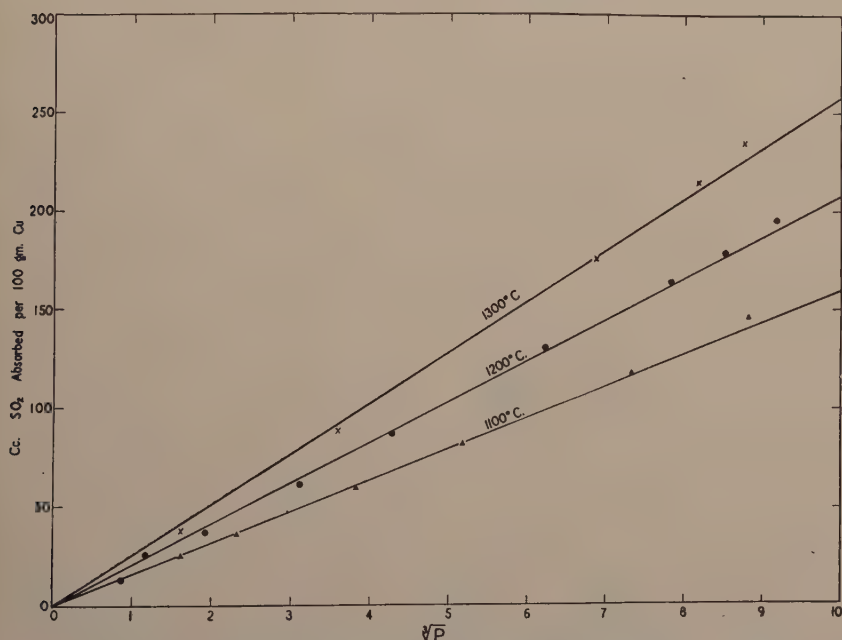


FIG. 4.—SOLUBILITY OF SULPHUR DIOXIDE IN PURE MOLTEN COPPER AS A FUNCTION OF CUBE ROOT OF PRESSURE.

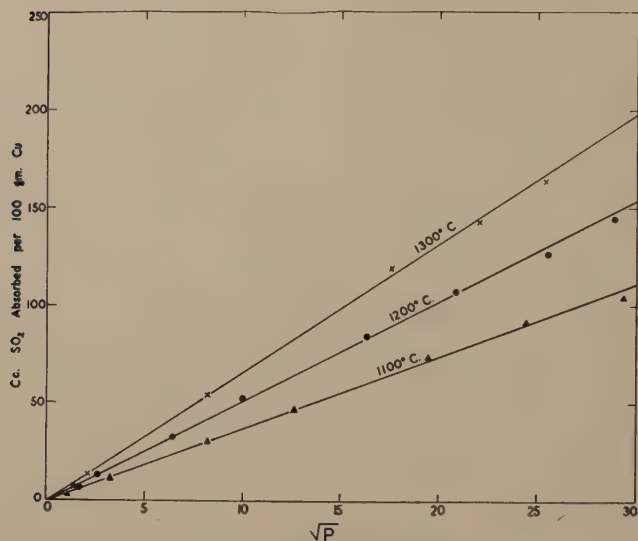


FIG. 5.—SOLUBILITY OF SULPHUR DIOXIDE IN MOLTEN COPPER CONTAINING AN EXCESS OF SULPHUR AS A FUNCTION OF SQUARE ROOT OF PRESSURE.

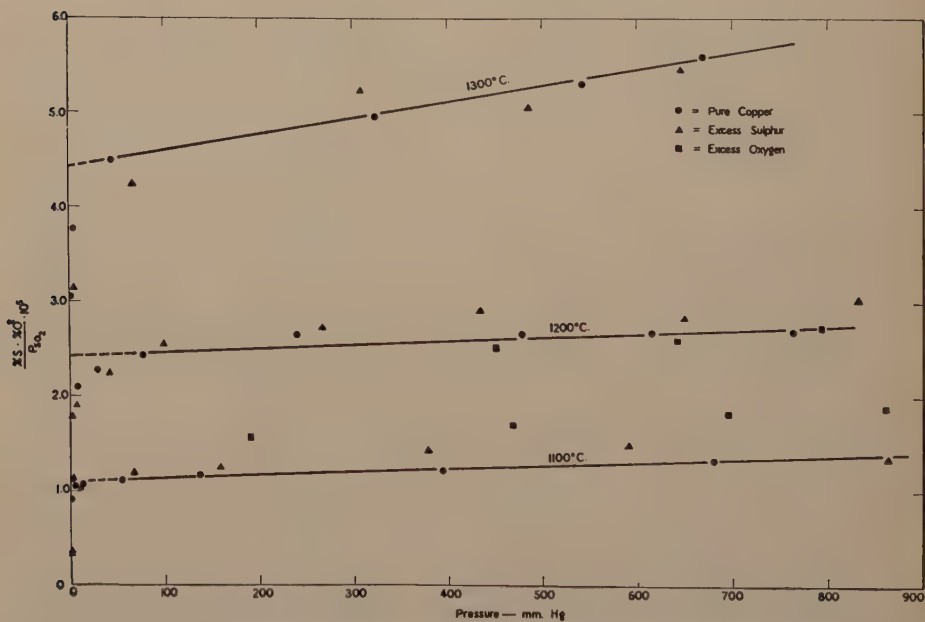


FIG. 6.—EQUILIBRIUM CONSTANTS FOR REACTION AS A FUNCTION OF PRESSURE.

fall away slightly toward the pressure axis, which can be accounted for on the basis that the last traces of carbon were not eliminated.

Calculations of Equilibrium Constant.—Neglecting the change in metal concentration, and considering that the concentrations of Cu_2S and Cu_2O are proportional to the percentage of sulphur and oxygen, respectively, the equilibrium constant for the reaction of solution given by Eq. 2 may be rewritten:

$$K' = \frac{\%S \times \%O^2}{P_{\text{SO}_2}} \quad [3]$$

Such an equilibrium constant has been calculated for each of the runs and is shown in the last column of the tables. The results have also been plotted against the pressure in Fig. 6. At very low pressures the equilibrium constant is low, which is to be expected since these values are greatly influenced by small partial pressures of CO in the system. In drawing the curves, the values for the pure copper runs have been given most weight, as it is felt that they are the more accurate. The values for the excess oxygen run at 1100°C . are somewhat above those for the pure copper and excess sulphur. This is believed to be due to slight crucible reaction. At 1200°C . the magnitude of the crucible reaction was approximated as previously discussed and the equilibrium constants were corrected accordingly, but it was impossible to make such a correction for the 1100° data. The way in which the lines have been drawn through the points for each temperature may be questioned, but the authors feel that they best represent the data.

The values for these and other runs not included indicate that there is a slight trend upward in the equilibrium constant with increasing pressure, the degree of this effect being greater at 1300°C . than at 1100° . Projecting each of the lines to intersect the ordinate, the values for the equilibrium constant of the reaction of solution

at very low pressures and infinite dilution are:

$$K = \frac{1100^\circ\text{C.}}{1.1 \times 10^{-5}} \quad \frac{1200^\circ\text{C.}}{2.4 \times 10^{-5}} \quad \frac{1300^\circ\text{C.}}{4.4 \times 10^{-5}}$$

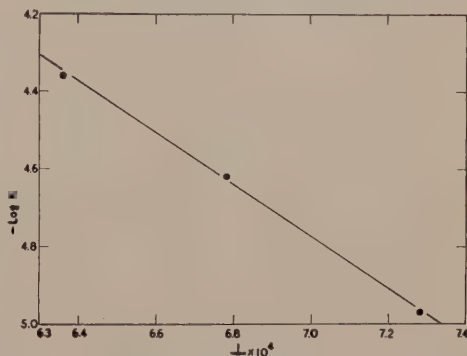


FIG. 7.—EFFECT OF TEMPERATURE UPON EQUILIBRIUM CONSTANT OF REACTION.

The increase in the ratio $\frac{\%S \times \%O^2}{P_{\text{SO}_2}}$ at higher pressures may be due to any of several causes, of which the two most probable are deviations from the laws of dilute solutions or increased reaction with the fused-silica tube. In either case the extrapolated values of K given above represent the best estimate of the true equilibrium constant of the reaction, defined by the expression

$$K = \frac{a_s \times a_o^2}{P_{\text{SO}_2}} \quad [4]$$

in which a_s and a_o represent the activities of sulphur and oxygen measured on such a scale that at very low concentrations $a_s = \%S$ and $a_o = \%O$.

If the deviations at higher pressures are ascribed to deviations from the simple solution laws, this may be expressed in terms of an activity coefficient defined as:

$$f_s = \frac{a_s}{\%S} \quad \text{and} \quad f_o = \frac{a_o}{\%O} \quad [5]$$

and related to the true equilibrium constant by the equation:

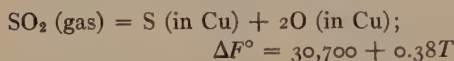
$$K = \frac{f_s \%S \times f_o^2 \%O^2}{P_{\text{SO}_2}} \quad [6]$$

The mean value of f_s and f_o can be calculated for any experimental point. At 1200°C . and 760 mm. pressure the mean value of f is found to be 0.97, indicating that a deviation of 3 per cent from the simple solution laws would account for the slope of the line in Fig. 5. The calculated deviations at the other temperatures are somewhat greater.

From the values of K at 1100° , 1200° and 1300°C ., the heat absorbed in the reaction may be calculated from the Van't Hoff equation:

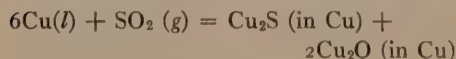
$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} \quad \text{or} \quad \log K = \frac{-\Delta H}{4.575T} + B \quad [7]$$

From a plot of the three values of $\log K$ against reciprocal temperature shown in Fig. 7, it is found that $\Delta H = 30,700$ cal. The increase in free energy in the reaction may be obtained from the same data and the result is expressed as follows:

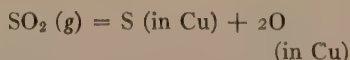


SUMMARY AND CONCLUSIONS

A study of the effects of carbon, oxygen and sulphur on the solubility of sulphur dioxide in molten copper at 1100° , 1200° and 1300°C . has been made. The results indicate that for pure copper and for copper containing an excess of either oxygen or sulphur, the reaction of solution may be expressed by either of the simple equations:



or



The equilibrium constant for this reaction has been determined at 1100° , 1200° and 1300°C .

Previous investigators concluded that the solubility of SO_2 in molten copper was

proportional to the square root of the pressure; a conclusion that was contrary to the recognized theories of solubility of gases in molten metals. It has been shown that this conclusion was false and that the system obeys the simple mass law. The discrepancies in previous work, including that published by the authors, resulted from the presence of very small amounts of carbon in the copper, which, because of the method used for measuring solubility, caused considerable error in the results.

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DISCUSSION

(S. Skowronski presiding)

S. SKOWRONSKI,* Perth Amboy, N. J.—The authors are to be congratulated on the courage of their convictions, and we are indebted to them for finally giving us the correct law on the solubility of sulphur dioxide in copper. However, to copper metallurgists the most important part of this paper is the fact that the authors definitely found that under certain conditions it is possible for carbon to exist in copper in sufficient amount to be determined. The amount of carbon found by the authors, 0.003 per cent, is more than a trace—it is an appreciable quantity, probably the largest single impurity in the copper they worked with—and it is no wonder that it affected the original results on the solubility of sulphur dioxide in copper that the authors gave us last year.

A few years ago the findings of the authors as to carbon would have been strongly disputed but evidence from different laboratories has been gradually accumulating that under certain conditions it might be possible for carbon to exist in copper, although no one had enough definite proof to warrant publication; so it remained for the authors to be the first to give a figure as to the actual amount of carbon that could be present in copper deoxidized with carbon.

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It is unfortunate that the authors did not present an original paper as to the presence of carbon, for this historical, as well as important, reference may be lost because it is not stated in the title of the paper.

A. J. PHILLIPS,* Barber, N. J.—I should like to congratulate the authors of this paper. I join with Mr. Skowronski in feeling that it has a great deal of practical significance.

Dr. Chipman, talking with me about a year ago, inquired rather pointedly about the solubility of carbon in pure copper. I did not think there was any, and brushed it aside rather lightly, I am afraid. Since that time a number of things have come up, each one of which has pointed toward the idea that there was some solubility of carbon in copper. While I am extremely reluctant to accept a new theory to explain known facts if a known older theory will explain the same facts, yet there is now so much circumstantial evidence that it is no longer safe to assume that carbon is insoluble in copper.

About a week before we received a copy of the paper by Floe and Chipman, we had set about to determine quantitatively the amount of carbon that is soluble in copper. I think there is no question whatever that a small amount of carbon is soluble, at least in liquid copper. We feel certain that the 0.003 figure is too high but the determination of 0.0004 per cent does not surprise us in the least.

The commercial and practical interest that carbon may have arises from the reaction of the carbon dissolved in copper plus oxygen dissolved in copper, giving carbon dioxide or monoxide, as the case may be.

In the literature on the solubility of various gases in copper, there are contradictory statements with regard to carbon monoxide and carbon dioxide. Those who determine the compositions of the gases taken from samples of copper usually state that carbon monoxide is soluble, since invariably they determine its presence. Those who try to dissolve carbon monoxide in copper say it is insoluble, and seem to prove their point.

Recently a British Institute of Metals paper by Pearson and Baker, entitled "Cause of Porosity in Tin-bronze Castings," indicated

that carbon monoxide was practically insoluble in the alloys examined and came to the conclusion that it was not harmful. In discussing that paper, Bolton disagreed with the authors in their conclusion. He stated that in practice the use of carbon monoxide is a constant source of trouble in tin bronzes and pointed out that if tin bronze is melted in an arc furnace, with a carbon monoxide atmosphere, the porosity in the castings is serious, and in his case was statistically determined by the number of leakers. He stated also that by admitting air under controlled conditions to the arc furnace and keeping the atmosphere slightly oxidizing, he wiped out much of the trouble from leakers, and he pointed out that if new metals were used, even in a carbon monoxide atmosphere, the first heats were seldom unsound. When the metal was circulated the trouble seemed to build up.

It seems to me that all the phenomena can be explained by the observations of Dr. Floe and Dr. Chipman that carbon is soluble in copper. When carbon is built up in the metal it can react with the oxygen picked up by the metal in pouring, forming carbon monoxide, which is insoluble and consequently causes gas trouble. There is some evidence to prove that the smallest trace of oxygen will react with carbon in copper, thus removing it. From this it seems evident that for tough-pitch copper we will still have to blame sulphur and hydrogen for gas trouble but for deoxidized copper and most of its alloys an understanding of the effect of carbon is most important.

C. S. SMITH,* Waterbury, Conn.—Now that the authors have demonstrated the solubility of carbon in copper, reactions involving carbon will be used to explain many phenomena hitherto explained differently. In particular, it seems likely that the unsoundness of copper melted under charcoal and poured in air can at least partly be attributed to carbon and need not be attributed entirely to hydrogen, as many of us have done in the past. I incline, however, to the belief that hydrogen is still an important agent in this connection and believe that the presence of water vapor along with carbon monoxide in furnace atmospheres is responsible for some of the conflicting results that have been published, particularly with the

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bronzes mentioned by Dr. Phillips in his discussion.

The authors melted copper in contact with silica and hydrogen. It is possible that some silicon might be reduced under these conditions and dissolved in the copper. Have the authors looked for such contamination?

G. P. SWIFT,* Cambridge, Mass.—I think the authors have started something they cannot stop. They must keep on for a while longer.

With regard to the present paper, was any attempt made to analyze the gases given off, to see whether carbon monoxide was present? In percentages as large as 2 c.c. in 30, it would indicate a gas analysis would show something.

OFHC copper contains appreciable amounts of manganese, silicon and iron. Would not some of these be effective with the use of excess oxide? The high temperature with the excess manganese might bring the reactions above, which indicated, as you stated, a crucible reaction. That might be manganese plus the copper oxide.

Were any check runs made using a copper comparatively free from carbon monoxide, such as the high-purity copper of American Smelting and Refining Co., or ordinary cathode copper?

C. A. FLOE AND J. CHIPMAN (authors' reply to discussion).—The authors are in agreement with Mr. Skowronski that one of the most important parts of this paper is that carbon was found to be soluble in copper in

appreciable amounts. Experimental work to determine this solubility is now under way.

The remarks by Dr. Phillips are very much appreciated, particularly because some of his experimental work has also confirmed the possible presence of carbon in copper. The authors agree that in deoxidized copper and copper-base alloys it is more likely that porosity is caused by the reaction between dissolved carbon and oxygen than by actual solution of carbon monoxide or carbon dioxide.

Dr. Smith agrees that porosity can be due to the reaction between dissolved carbon and oxygen when copper or copper-base alloys are poured in air. It is true that hydrogen undoubtedly is also a factor. Dr. Smith mentions the possibility that silicon may have entered the melt by reduction of the fused silica tube with the hydrogen used for deoxidation. This possibility was considered. However, analysis of an ingot after reduction with hydrogen at 1200°C. showed the silicon present to be only a trace, indicating that such reduction does not take place.

In reply to Mr. Swift, it was not possible in the apparatus used to analyze any of the gases given off during melting. However, the authors do not know of any gases other than carbon monoxide or dioxide that would cause the pressures that were developed in the system. The reactions mentioned by Mr. Swift, such as manganese reacting with copper oxide, would not form gases, and therefore could not generate any pressures.

* Massachusetts Institute of Technology.

Self-diffusion of Copper

BY MARTIN S. MAIER* AND H. R. NELSON†

(New York Meeting, February 1942)

THE diffusion of metals plays an important role in many metallurgical processes,^{1,2} as, for example, the formation of alloys by the annealing of mixed powders, the homogenization of segregated alloys, and the carburization of steel. Other equally important phenomena, such as recrystallization and creep, are based on the movement of like atoms. Although much is known concerning the effects of diffusion in metals, very little is known concerning the details of the physical processes involved.^{1,3-5} The data that should give most information concerning the processes involved in diffusion are those on the diffusion of like atoms—self-diffusion.

Very little is known concerning the rates of self-diffusion of metals because before the discovery of artificial radioactivity in 1934 there was no means of detecting the movement of the diffusing atoms through the solvent metal except in the elements possessing natural radioactive isotopes—lead, thallium and bismuth.

Using the induced radioactivity of the element as an indicator, atoms can now be "tagged" so that the rate of diffusion of the radioactive isotopes of an element (tagged atoms) into the stable isotopes of the same element can be measured. As the radioactive and stable isotopes of an element differ only in nuclear structure, it is quite certain that all isotopes of an element diffuse at the same rate.

Two techniques have been used to measure self-diffusion. In one, a thin layer of radioactive metal is deposited on the face of the solvent metal, and the decrease in the surface activity as the radioactive atoms diffuse into the solvent metal is measured. This method has been used to determine the coefficients of self-diffusion of lead⁶⁻¹⁰ and bismuth¹⁰ using natural radioactive isotopes, and of gold¹¹ and copper¹² using artificial radioactive isotopes. In the other technique a thin layer of the radioactive metal is deposited on one face of the solvent metal, and after diffusion has occurred the specimen is cut in thin sections to obtain the concentration-penetration curve. This method has been used to determine the coefficients of self-diffusion of gold,¹³ zinc,¹⁴⁻¹⁶ silver,¹⁷ and copper.¹⁸ The second method was used for the work described in this paper.

MATERIALS

The coefficients of self-diffusion were determined in two grades of polycrystalline copper and in single crystals of copper. Commercial OFHC copper was used in the form of disks 1 in. in diameter by $\frac{1}{8}$ in. thick. Samples of high-purity copper described by Phillips and Skinner¹⁹ were supplied through the courtesy of the American Smelting and Refining Co. The high-purity copper rod was used without remelting by cross-rolling to a thickness of 0.075 in., from which disks $\frac{7}{8}$ in. in diameter were cut. A good grade of bus-bar copper was used to make the single crystals.

Manuscript received at the office of the Institute Sept. 12, 1941. Issued as T.P. 1419 in METALS TECHNOLOGY, January 1942.

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† Assistant Supervisor, Battelle Memorial Institute.

¹ References are at the end of the paper.

EXPERIMENTAL METHOD

The radioactive copper, Cu^{64} half-life 12.8 hr., was prepared by deuteron bombardment of copper in a cyclotron.²⁰ The copper was dissolved in nitric acid to form copper nitrate, which was evaporated nearly to dryness to drive off the excess nitric acid. The copper nitrate crystals were redissolved in water with enough nitric acid added to form a clear solution. About 200 c.c. of solution was necessary for electroplating. The radioactive zinc, Zn^{65} also produced by the deuteron bombardment of copper was not extracted from the copper because its yield was negligible compared to that of copper.²¹

The radioactive copper was electroplated onto the specimens to a thickness of about 10^{-4} cm. The anode was a $\frac{1}{2}$ -in. loop of platinum wire. A current of 10 to 12 ma. for 30 to 40 min. was used. The plated specimen was then placed inside a massive copper holder into which was inserted the hot junction of the temperature-measuring thermocouple. A second thermocouple placed beside the copper holder was connected to a potentiometric controller, which maintained the specimen at the desired temperature $\pm 1^\circ\text{C}$. The specimen was heated, by means of an electric furnace, in a quartz tube, which was kept at about 10^{-4} mm. pressure by continuous evacuation. The furnace was hot when the evacuated quartz tube containing the specimen was inserted, and the specimen was rapidly cooled at the end of the diffusion period by quenching in water. The concentration of radioactive copper at various distances was determined by machining off successive layers 0.001 in. thick in a lathe and measuring the activity of the chips with a Geiger-Müller counter. The concentration of the radioactive copper was expressed as the activity (counts per minute) per milligram of copper. The thickness of each layer was calculated from the weight of the chips

and the density of copper. The specimen was weighed before and after machining, and in all tests the total weight of the chips equaled over 99 per cent of the metal removed from the specimen.

THEORY

It is assumed that self-diffusion follows Fick's law,²²

$$\frac{dC}{dt} = D \frac{d^2C}{dx^2} \quad [1]$$

where C is the concentration of the diffusing metal at the distance x at the time t , and D is the diffusion coefficient representing the amount of metal in grams diffusing in one second across an area of 1 sq. cm. through a unit concentration gradient.*

In the solution of the diffusion equation the solvent metal is considered as a semi-infinite sheet, since no metal diffuses to the far face and a negligibly thin layer of diffusing (radioactive) metal is deposited on the front face. Under these conditions the solution of Eq. 1 is²³

$$C = \frac{C_0}{2\sqrt{\pi Dt}} e^{-x^2/4Dt} \quad [2]$$

where C_0 is a constant depending on the amount of radioactive copper plated on the surface.

Knowing the concentration of radioactive copper at different distances, it is convenient to find the diffusion coefficient D by graphical methods. Taking logarithms of Eq. 2,

$$\log C = \log \frac{C_0}{2\sqrt{\pi Dt}} - 0.4343 \frac{x^2}{4Dt}$$

* In many diffusion processes, the diffusion constant D varies with the concentration of the solute and consequently Fick's law becomes approximately valid only if the range of concentrations is kept small. Fick's law is an exact description of the self-diffusion process because the "solute atoms" are identical with the "solvent atoms" in all respects except that they are tagged.

or, since the first term on the right is a constant for a given experiment,

$$\log C = \frac{-0.1086}{Dt} x^2 + \text{constant} \quad [3]$$

If $\log C$ is plotted against the distance squared, a straight line of slope $\frac{-0.1086}{Dt}$

will be obtained, from which D is calculated. Since the diffusion takes place at elevated temperatures, and the concentration-penetration curve is obtained at room temperature, it is necessary to consider the thermal expansion of the metal. At the temperatures used in these experiments, there was an expansion of about 1 per cent.

Dushman and Langmuir²⁴ treated the diffusion process as analogous to a chemical reaction, in that the diffusing atom must possess a certain energy of activation before it can surmount the potential barrier that it encounters in the solvent metal. They obtain the equation relating D and t ,

$$D = Ae^{-Q/RT} \quad [4]$$

where D is the diffusion coefficient, Q the energy of activation, R the gas constant, T the absolute temperature, and A a constant.

Dushman and Langmuir make an assumption concerning the constant A ; namely, $A = Q\delta^2/Nh$ where δ is the interatomic jump distance, N Avogadro's number and h Planck's constant. The Dushman-Langmuir equation can then be written

$$D = \frac{Q\delta^2}{Nh} e^{-Q/RT} \quad [5]$$

DIFFUSION IN POLYCRYSTALLINE COPPER

A typical curve obtained when plotting the logarithm of the concentration of the radioactive copper (counts per minute per milligram of copper) against the square of the distance of penetration is shown in Fig. 1. These data were obtained from a sample of high-purity copper held at a

temperature of 950°C. for 10 hr. 5 min. Since the points fall on a straight line, the solution of the differential equation is correct. The straight line has a slope of $-3.40 \times 10^3 \text{ cm.}^{-2}$, which gives $D = 8.92 \times 10^{-10} \text{ sq. cm. per second}$.

The dependence of the diffusion coefficient on temperature is shown in curve I, Fig. 2, in which the logarithm of D is plotted against the reciprocal of absolute temperature. The straight line indicates that D varies with temperature according to the relation expressed in Eq. 4. The points indicated by open circles are the results of experiments on single specimens of OFHC copper. The points indicated by the solid dots are the averages of the results obtained by placing two disks of the high-purity copper in the holder at the same time. The difference between the two individual values of D amounted in each case to less than 2 per cent. All points fall on the same straight line, which indicates that the rate of diffusion is independent of the purity of the copper within the range of purity of the samples used. This was pointed out by Steigman, Shockley and Nix,¹² who also concluded that the rate of diffusion is independent of grain size.

DIFFUSION IN SINGLE CRYSTALS

The diffusion in single crystals was studied to furnish data for comparison with the results on polycrystalline copper and also as a search for anisotropy of diffusion.

Anisotropy of diffusion in noncubic metals has been observed by several investigators^{10,15,25} but the results with cubic metals are not conclusive. Experimental evidence for the anisotropy of diffusion of copper into aluminum²⁶ and zinc into copper²⁷ has been reported, but from theoretical considerations Mehl and McCandless²⁸ conclude that diffusion in cubic crystals must be isotropic on a macroscopic scale.

A good grade of bus-bar copper was melted in a graphite crucible in a vacuum furnace and allowed to cool slowly in a temperature gradient. This method, de-

The diffusion coefficients in the single crystals were determined by the same technique as were those in the polycrystalline copper. Two specimens, one with

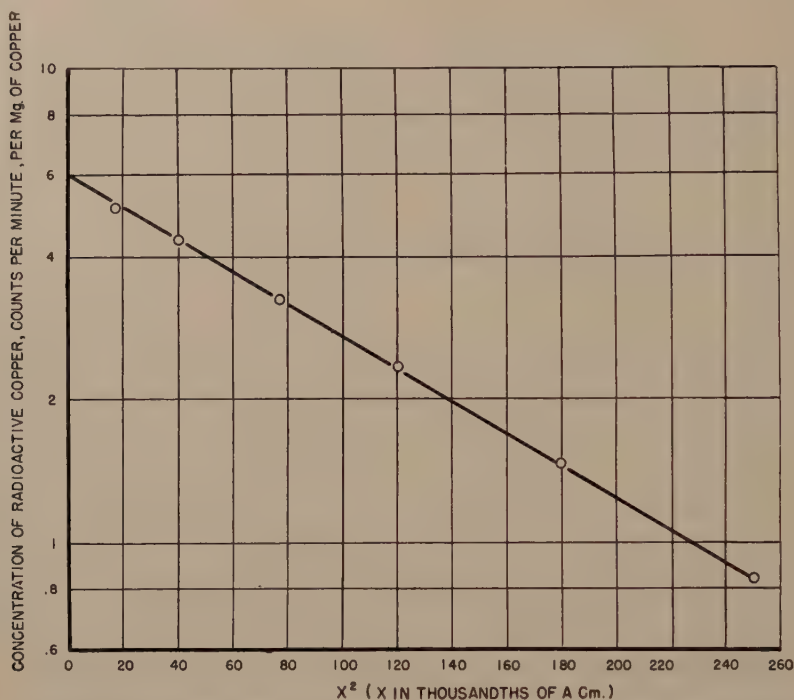


FIG. 1.—CONCENTRATION-PENETRATION CURVE FOR DIFFUSION OF RADIOACTIVE COPPER INTO COPPER DURING 10 HOURS 5 MINUTES AT 950°C.

Logarithm of concentration is plotted against depth of penetration squared.

scribed by Thompson,²⁹ yielded single crystals about 3 in. long by 1 in. in diameter. After determination of the crystal orientation by etching,²⁹ each crystal was cut in a milling machine into slabs whose faces were successively polished and etched to remove the polycrystalline layer left by the milling cutter. Two sets of single-crystal slabs were thus prepared, one with faces parallel to a (100) plane, the other with faces parallel to a (110) plane. The orientation was checked by back-reflection Laue pictures, and in no case was the orientation off by more than 4°.

face parallel to a (100) plane and the other with face parallel to a (110) plane, were inserted in the furnace at the same time, with the plated faces together. Thus any difference in the diffusion in the two crystals would be due to anisotropy or to other characteristics of the crystals themselves rather than to any possible temperature difference.

The dependence of the diffusion coefficient in single crystals of copper on temperature is shown in curve I, Fig. 3. In some experiments the diffusion coefficients for the two crystal orientations were quite different and the two values

were plotted separately. In other cases crystalline. The results from that experiment, were discarded.

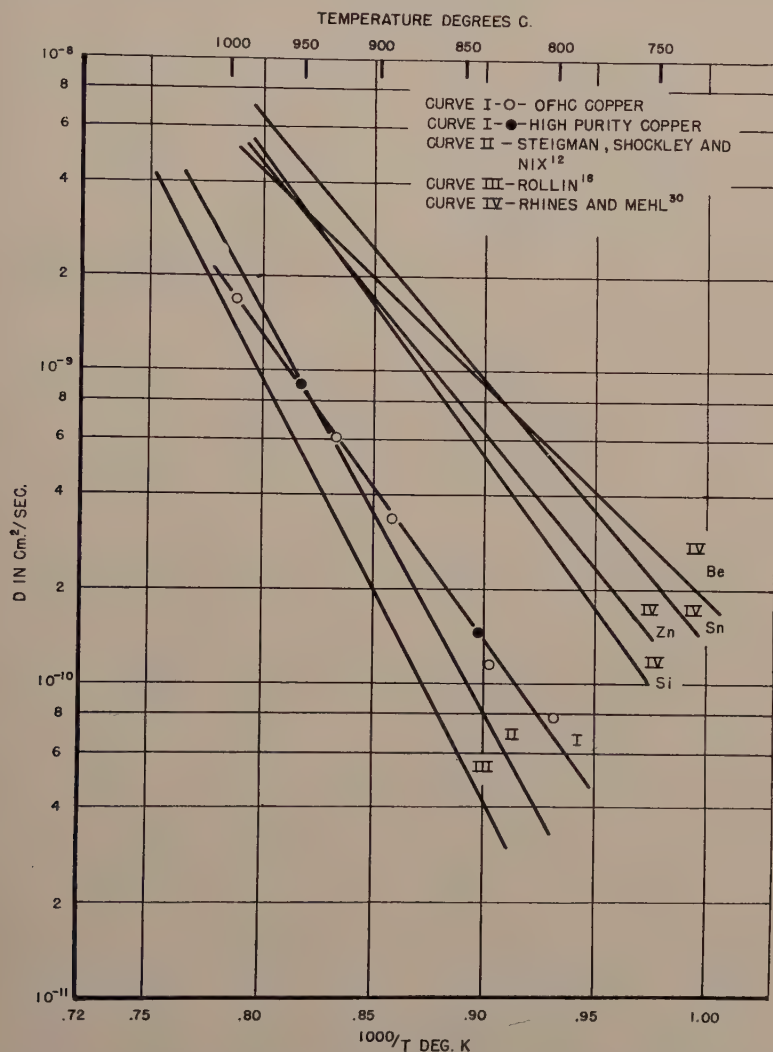


FIG. 2.—VARIATION OF D IN POLYCRYSTALLINE COPPER WITH TEMPERATURE.

Logarithm of D is plotted against reciprocal of absolute temperature, square centimeters per second.

Open circles indicate results of experiments on single specimens of OFHC copper; solid circles are averages of results obtained by placing two disks of high-purity copper in the holder at the same time. Straight line indicates that D varies with temperature according to equation 4.

identical and these values are indicated by a single point. After each experiment, the crystals were etched to check for recrystallization. In one case the copper had recrystallized and had become poly-

CONSTANTS OF SELF-DIFFUSION OF COPPER

The energy of activation Q and the constant A of Eq. 4 can be calculated from the slopes of the straight lines in Fig. 3. By using Eq. 5, these constants can be

calculated also from the diffusion coefficient at a single temperature provided δ , the of 2 produces a change of only about 2 per cent in the calculated value of Q .

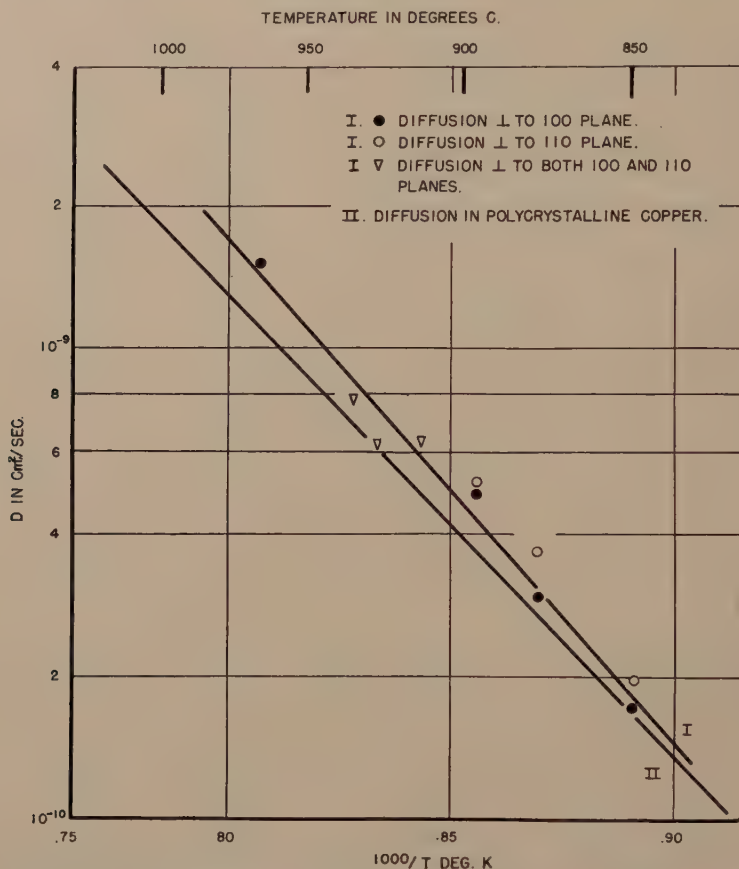


FIG. 3.—VARIATION OF D IN SINGLE CRYSTALS OF COPPER WITH TEMPERATURE.

Logarithm of D is plotted against reciprocal of absolute temperature, square centimeters per second.

"jump distance," is known. For the calculations giving the values in Table I, δ was taken as the distance of closest approach of the atoms, 2.55\AA .

The values of Q calculated from the Dushman-Langmuir equation agree fairly well with those obtained from the plot of $\log D$ vs. $1/T$ but they vary somewhat with the temperature chosen in making the calculations. It should also be mentioned that, in using the Dushman-Langmuir equation, a change in D by a factor

DISCUSSION OF RESULTS

The accuracy of the results depends mainly on the accuracy with which the slope of the concentration-penetration curve can be obtained. When this line is relatively flat, as in Fig. 1, the error in slope amounts to about 2 per cent, but at low temperatures, where the line becomes rather steep, this error may reach 15 per cent or even more. The statistical error in measuring each point of the curve varied from 2 to 3 per cent.

The error in depth due to chips lost during machining amounts to less than 1 per cent. The diffusion times were corrected for the time of heating and cooling, and are accurate to within 1 per cent. The temperature was kept constant to within $\pm 1^\circ\text{C}$.

results as a whole are inconclusive as regards isotropy. It seems apparent, however, that if anisotropy of diffusion exists, its effects are small and are likely to be masked by lineage and other imperfections in the crystal lattice.

TABLE 1.—*Constants of Self-diffusion of Copper*

	A, Sq. Cm. per Sec.	Q, Cal. per Mol	Temperature, Deg. K	Methods of Calculation ^a	Reference
Polycrystalline.....	0.10	45.1		1	Present work
Polycrystalline.....	11.	57.2		1	12
Polycrystalline.....	47.	61.4		1	18
Polycrystalline.....	0.32	47.6	1075	2	Present work
Polycrystalline.....	0.33	48.1	1266	2	Present work
Polycrystalline.....	0.9 ^b	51.0	1223	2	12
Single crystals.....	0.6	49.		1	Present work
Single crystals.....	0.32	47.6	1111	2	Present work
Single crystals.....	0.32	47.3	1250	2	Present work

^a 1 indicates A and Q determined from log *D* vs. 1/*T* curve; 2, A and Q calculated from Dushman-Langmuir equation.

^b This value of A from reference 12 seems to be in error unless the value of δ in Eq. 5 is taken considerably larger than the lattice constant for copper. With $\delta = 2.55\text{\AA}$., distance of closest approach, and using the data of reference 12, A = 0.33 sq. cm. per second.

and an error of 1°C . produces an error of 2 per cent in the value of *D*. Another source of error is the absorption of radiation in the copper chips. When the chips are uniform in size and shape, the absorption is the same in all samples and the error is negligible. Considerable care was taken to use the same sharp pointed tool in sectioning all specimens and it is believed that the absorption errors were negligible.

Since all of these errors are independent it is estimated that the values of *D* are accurate to about 5 per cent at the higher temperatures and 15 per cent at the lower temperatures.

The scatter of the points obtained with single crystals has not been completely explained. Since the scatter is considerably more than the experimental error, it is probably due to differences in the perfection of the lattice in the various crystals. This conclusion is supported by the back-reflection Laue photograms, which showed considerable evidence of lineage structure. Although in three experiments the rate of diffusion in the [110] direction was greater than in the [100] direction, the

Since all the points obtained with single crystals lie above the diffusion curve for polycrystalline copper, diffusion was faster in the single crystals. With the reasonable assumption that lattice imperfections increase the rate of diffusion, the results indicate that the single crystals were less perfect than individual crystals in the polycrystalline copper. Cold-working strains were practically eliminated from the polycrystalline samples by annealing but ordinary annealing does not eliminate lineage imperfections.

The available data on the self-diffusion coefficients of copper are given in Fig. 2. The diffusion coefficients from the present work are considerably higher than those obtained by Rollin¹⁸ and are higher than the values given by Steigman, Shockley and Nix¹² for lower temperatures. The activation energy obtained from the present data, however, is considerably lower than the values obtained in those earlier investigations, as is shown in the first three columns of Table 1. Since different experimental methods were used for the three investigations, it is difficult to

explain these discrepancies. It should be mentioned, however, that, within the limits of their experimental error, the data obtained by Steigman, Shockley and Nix are in agreement with these in the temperature range above 850°C.

Rhines and Mehl³⁰ measured the coefficients of diffusion of various metals into copper and extrapolated their results to zero concentration of solute. Their curves (IV in Fig. 2) were all similar and Rhines and Mehl suggested that they represented the self-diffusion coefficient of copper. While the actual rates of self-diffusion appear to be much lower than their results indicate, it is noteworthy that the activation energy for self-diffusion obtained in the present work is close to the highest activation energy obtained by Rhines and Mehl for various solutes.

SUMMARY

Radioactive copper has been used to study self-diffusion in polycrystalline copper and in single crystals of copper. The rate of diffusion was higher in single crystals than in ordinary polycrystalline copper. The results are inconclusive regarding the possible anisotropy of self-diffusion in copper because of erratic results attributed to lineage or other imperfections in the single crystals. It was concluded, however, that if anisotropy of diffusion exists it must be small and easily masked by effects due to crystal imperfections.

ACKNOWLEDGMENT

The authors are indebted to the Department of Physics of the Ohio State University and to Dr. M. L. Pool for supplying the radioactive copper and to Mr. O. J. Huber and Dr. C. M. Schwartz for assistance in the preparation of the single crystals. They also wish to express appreciation of the friendly interest of Dr. Edward Mack, under whose supervision this investigation was started.

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DISCUSSION

(C. E. Swartz presiding)

C. H. SAMANS,* Southbridge, Mass.—There are two points I should like to raise in connection with this very interesting work on self-diffusion. The first concerns the differences the authors have found between values of D normal to (100) and (110) planes of single crystals. While we know virtually nothing about the exact mechanism of diffusion, we do know that it must proceed by atoms moving from one lattice position to another, probably the closest one. For the face-centered cubic lattice there are 12 of these "closest" positions to which a diffusing atom could "jump," and in the present case any one of them is a possibility. However, only jumps to certain of

* American Optical Co.

these positions will result in a movement forward, into the crystal.

In movement normal to a (110) plane, a single forward jump could bring the diffusing atom either to a position $\frac{\sqrt{2}}{2}a_0$ away from

the original surface or to one $\frac{\sqrt{2}}{4}a_0$ away.

The average distance it would move into the crystal, then, would be $0.53a_0$. However, in diffusion normal to (100), any forward move-

ment would bring it to a position $\frac{a_0}{2}$ from the

original surface, a distance about 6 per cent less.

Since in either case the frequency at which a jump occurs must be identical, would not a slightly higher rate of diffusion be expected for movement normal to the (110) plane than for that normal to (100)? Accordingly, if this reasoning is correct, the authors are justified only in concluding that diffusion was faster in single crystals of these two orientations than it was in polycrystalline material.

The second point concerns the recrystallization of one of the crystals after diffusion. While, apparently, great care was taken to remove any disturbing effects of the machining, I wonder whether the results themselves do not indicate that it may not have been sufficient? I can think of no reason except strain why a single crystal should recrystallize during self-diffusion. There certainly should be no phase change involved.

Copper crystals are not very strong and can readily be disturbed even by quite small stresses. Both Burghoff and Elam found that 70-30 brass, which is much stiffer, will be strained to an appreciable depth during cutting. The most satisfactory way of showing this is to anneal the specimen carefully at a comparatively high temperature after the machining is completed. This causes the strained areas to recrystallize, and enables them to be removed by a combination of careful and alternate polishing and etching similar to the method used by the authors. However, even after this treatment it is advisable to reanneal in order

to be sure that the handling has done no harm. The additional anneal could do no harm to an unstrained single crystal, and would prevent possible undesirable strains. Since copper is so much softer than brass, I should think that such treatment might be even more important with it.

On page 42 the authors remark ". . . and etched to remove the polycrystalline layer left by the milling cutter." This statement is somewhat puzzling, especially in view of the foregoing remarks. They make no mention of any previous anneal, yet they secure a polycrystalline layer. Does this signify: (1) that they meant a "disturbed" layer; (2) that sufficient heat was developed during milling to recrystallize the surface; or (3) that the specimen was annealed, although no mention was made of it? In any case, I would suggest annealing such single crystals at least once after the final work is done on them, in order to ensure satisfactory removal of all residual strains.

M. S. MAIER AND H. R. NELSON (authors' reply).—The anisotropy of diffusion in the two crystal orientations, as discussed by Dr. Samans, is the effect we were seeking when the diffusion coefficients were determined in the single crystals. Since there was no regularity in the diffusion coefficients in the two crystal orientations, we concluded that the difference was not due to anisotropy but rather to some other factor or factors, of which strains might be an important one. If there is some anisotropy of diffusion in copper, the effect is small, and is easily masked by other factors.

Annealing of single crystals was considered an unnecessary procedure as the annealing time would be small compared with the time during which diffusion took place. Thus strains would be eliminated early in the diffusing period, and the greater part of the diffusion would take place in an unstrained crystal.

Concerning the question raised by Dr. Samans about the "polycrystalline layer left by the milling cutter," perhaps "disturbed layer" would be a better term.

Effect of Iron, Cobalt and Nickel on Some Properties of High-purity Copper

By J. S. SMART, JR.,* JUNIOR MEMBER, AND A. A. SMITH, JR.,* MEMBER A.I.M.E.

(New York Meeting, February 1942)

NUMEROUS investigations of the effects of the various impurities common to commercial coppers have been published, and the data have found wide use in industry. Naturally, emphasis has been placed on the oxygen-bearing coppers of the tough-pitch variety, but need is now evident for data covering the oxygen-free condition as well. Furthermore, relatively few of the important reactions between oxygen and the various impurities are well understood, and often the data at hand are not applicable to the low concentrations encountered in commercial coppers.

This paper presents the changes in conductivity and softening temperature derived from individual additions of the group VIII triad, iron, cobalt and nickel, to high-purity copper, and constitutes a portion of the copper-research program being conducted at the Central Research Laboratory of the American Smelting and Refining Co. The method of preparation of high-purity copper and its alloys in either the oxygen-free or oxygen-bearing form has been described previously.¹ The purity of this material, and the methods developed to produce it, provide the means for direct investigation of the very low concentration range in which the various impurities generally exist in commercial coppers. The usual necessity for extrapolation to this range using the results obtained from higher concentrations, and

the interfering effects of extraneous impurities, are thus simultaneously circumvented. Since previously published data have adequately presented the effects of higher concentrations of iron, cobalt and nickel, the present investigation has been confined to the composition range 0 to 0.05 per cent.

All alloys were initially prepared in the form of oxygen-free continuous cast rod, the weighed alloying additions in suitable form being charged with the pure copper to the continuous casting crucible. The best of the available high-purity alloying materials were used, and spectrographic analyses confirmed the absence of interfering elements from the alloys formed. Each series was compounded in the direction of increasing concentration, starting with pure copper in a new crucible and finishing with the 0.05 per cent alloy. Composition was closely controlled by adding the alloying element in the form of a carefully compounded and analyzed master alloy rendered uniform by continuous casting. The accuracy of this method of synthesis was proved by chemical analysis of the more concentrated alloys, and, accordingly, there is every reason to credit the stated composition of the very dilute alloys in the range where chemical analysis becomes highly uncertain.

Oxygen-free samples for measurements of conductivity and softening temperature were obtained by drawing the continuous cast rod to wire of 0.081-in. diameter, employing a number of intermediate anneals to refine the grain structure. The

Manuscript received at the office of the Institute Nov. 6, 1941. Issued as T.P. 1434 in METALS TECHNOLOGY, February 1942.

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¹ References are at the end of the paper.

iron alloys were prepared some months earlier than the nickel and cobalt series, and were cast in the form of $\frac{5}{16}$ -in. diameter rod. With this initial diameter three intermediate anneals ($\frac{1}{2}$ hr. 600°C . in H_2) were employed at diameters of 0.257, 0.204 and 0.162 in., and the final cold reduction to 0.081 in. was 75 per cent. Shortly thereafter the diameter of the cast rod was increased to $\frac{3}{8}$ in., and for the nickel and cobalt alloys an additional intermediate anneal was inserted at 0.3125 in., the remainder of the drawing schedule remaining the same.

The method employed for determining the softening temperature has been discussed; it depends on the determination of the temperature corresponding to the half-hard point. Briefly, the procedure involves the determination of the tensile strengths in the hard-drawn condition (75 per cent cold reduction) and after a 1-hr. anneal at 500°C ., which is defined as the annealed condition. The mean of these extremes is defined as the half-hard point. A sufficient number of 1-hr. anneals at suitable temperatures in a controlled oil bath provide the necessary data for plotting

TABLE 1.—*Alloys of Iron and Pure Copper*

Sample No.	Fe, Per Cent	O_2 , Per Cent	Hard Drawn	Conductivity, Per Cent I.A.C.S., Annealed at						Softening Temperature, Deg. C.
				300°C .	400°C .	500°C .	600°C .	700°C .	800°C .	
69M	Nil	Nil	100.1	102.3	102.3	102.25	102.3	102.25	102.3	142
68M	0.00007	Nil	100.0	102.1	102.15	102.2	102.2	102.2	102.2	150
57M	0.0003	Nil	99.85	102.0	102.0	102.0	102.0	102.05	102.15	140
56M	0.0007	Nil	99.7	101.7	101.8	101.8	101.8	101.9	101.9	160
55M	0.0015	Nil	99.15	101.2	101.25	101.25	101.3	101.25	101.25	143
54M	0.0054	Nil	96.05	98.1	98.05	98.1	98.1	98.1	98.0	153
53M	0.0105	Nil	93.1	95.15	94.95	95.0	95.0	94.95	94.75	162
52M	0.05	Nil	76.3	80.5	79.05	78.25	78.2	78.1	78.0	167
69MO	Nil	S ^a	100.2	102.2	102.25	102.2	102.25	102.25	102.2	138
68MO	0.00007	S	100.2	102.2	102.25	102.3	102.3	102.3	102.25	138
57MO	0.0003	S	100.2	102.2	102.2	102.3	102.3	102.3	102.25	137
56MO	0.0007	S	100.2	102.2	102.25	102.25	102.3	102.3	102.25	137
55MO	0.0015	S	100.2	102.15	102.25	102.2	102.2	102.2	102.2	138
54MO	0.0054	S	100.1	102.15	102.2	102.2	102.2	102.2	102.15	139
53MO	0.0105	S	100.1	102.1	102.15	102.15	102.2	102.1	102.2	138
52MO	0.05	S	99.9	101.95	102.05	102.0	102.0	102.0	102.0	148

^a Saturated with oxygen by diffusion at 850°C .

Samples for conductivity measurement were annealed for one hour in a specially constructed tube furnace equipped with automatic temperature control ($\pm 1^{\circ}\text{C}$). Anneals were performed at 100°C . intervals between 300° and 800°C . for each alloy, using a hydrogen atmosphere for oxygen-free samples and purified nitrogen for oxygen-bearing wires. All samples were quenched from the furnace into a 10 per cent H_2SO_4 pickle bath. Conductivities (per cent I.A.C.S.) were determined by means of a Hoopes bridge having an accuracy of ± 0.1 per cent, readings from which had previously been found to check the results obtained from a Kelvin bridge.

the portion of the curve passing through the half-hard range, and the softening temperature is then determined graphically.

EFFECT OF IRON

The earlier investigations of the effect of iron on the conductivity of copper carried out by Addicks,² Skowronski,³ and Hansen and Ford⁴ were confined to the composition range above 0.02 per cent Fe. Oxygen was present in all the samples, and, as pointed out by Heuer,⁵ a large part of the iron present was rendered insoluble by the formation of an iron oxide. Heuer⁵ and Linde⁶ succeeded in removing most of

the oxygen from their melts, and obtained a far greater loss of conductivity per unit of iron added. The data of this paper, representing very highly deoxidized alloys,

ature is probably minute. Tammann and Oelsen⁷ have derived a formula for the solubility curve, based on magnetic measurements at higher concentrations, which

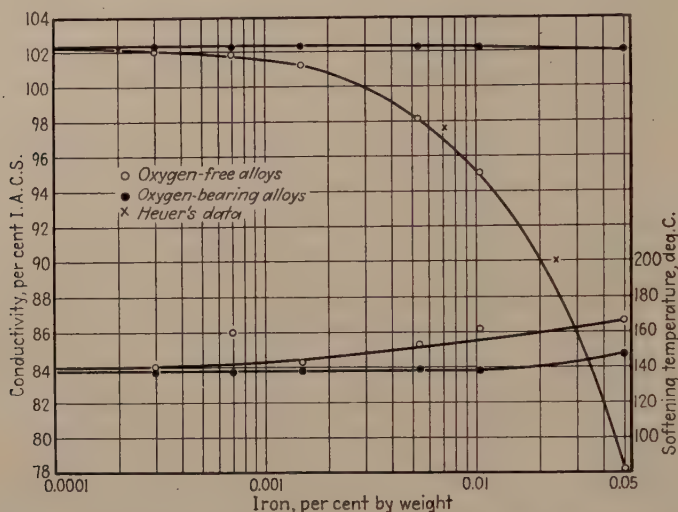


FIG. 1.—EFFECT OF IRON ON CONDUCTIVITY AND SOFTENING TEMPERATURE OF HIGH-PURITY COPPER.

again revise the effect of iron upward, as shown in the oxygen-free data of Table I and Fig. 1. Although it may be considered doubtful that the conductivity losses are a linear function of iron content over even a limited composition range, the present data when plotted on rectangular coordinates, using either atomic or weight per cent, are well represented by a straight line from 0 per cent Fe to at least 0.005 per cent Fe. Between these limits the loss of conductivity amounts to 0.80 per cent I.A.C.S. for each 0.001 per cent Fe present. Above 0.005 per cent Fe the unit effectiveness of iron consistently decreases.

With the exception of the 0.05 per cent Fe samples all other alloys exhibit uniform conductivities over the annealing range, behaving as true solid solutions. At 300° and 400°C. an appreciable increase in conductivity indicates precipitation of iron from the 0.05 per cent alloy, and the equilibrium solid solubility at this temper-

places the solubility value at 300°C. at 3.89×10^{-4} per cent Fe by weight. The long-time annealing program necessary to corroborate this approximation by conductivity measurements has not been included in the present study.

Because iron oxide has a tendency to segregate from liquid copper, the oxygen-bearing alloys were not prepared by remelting the oxygen-free rod under oxidizing conditions, but by oxidation of the iron *in situ* by exposure to oxygen at 850°C. for the period required for saturation. In practice the $\frac{5}{16}$ -in. cast rods were first allowed to acquire an oxide coating in the furnace, then were protected from excessive scaling by flushing with nitrogen for the duration of the diffusion process. Proof samples were withdrawn occasionally and prepared for conductivity measurement, to follow the course of the reaction. Typical results are illustrated by the behavior of the 0.05 per cent Fe sample, as follows:

TIME OF DIFFUSION AT 850°C., Hr.	CONDUCTIVITY—0.05 PER CENT FE-PURE CU, PER CENT I.A.C.S.
0	78.25
24	93.65
48	98.5
72	102.0
96	102.0

The precipitation of iron as an oxide proceeds to completion in the presence of only very small quantities of oxygen, with full restoration of the conductivity to that of pure copper, except for the sum of the small volume effect to be expected from the presence of inert iron oxide, and the slight loss due to solid solution of oxygen. The extent of the deoxidizing properties of iron previously noted by Hansen and Ford is thus seen to be of considerable magnitude. Rhines⁸ has identified the oxide as Fe_3O_4 by X-ray methods, and in the present research an indirect confirmation of this result was obtained by oxidizing a 2 per cent Fe alloy, in the form of rolled strip, to completion at 850°C. The annealed and oxidized sample responded readily to the attraction of a permanent magnet, suggesting the presence of magnetite.

Iron frequently has been classed among those elements most effective in increasing the softening temperature of strain-hardened copper,^{4,9,10} but these observations were made on alloys containing upward of 0.5 per cent Fe. The effect of small amounts, such as are encountered in commercial coppers, is decidedly minute (see Table 1 and Fig. 1), irrespective of whether the iron is present in solid solution or precipitated as Fe_3O_4 . Probably a substantial increase in the slope of the curve of Fig. 1 does occur at higher concentrations, but as far as the copper industry is concerned these would constitute special alloys.

In regard to the tough-pitch coppers, there is little question that the small amounts of iron present are mechanically suspended particles of Fe_3O_4 having negligible effects on the conductivity and annealing characteristics. On the other

hand, the conductivity of oxygen-free copper is reduced appreciably by even the small quantities of iron contained in the normal commercial coppers; in contrast to this, there is scant possibility that the effects on the softening temperature could be anything but negligible.

EFFECT OF NICKEL

Nickel is known to form an oxide in the cupronickels, and has been detected in this form by Archbutt and Prytherch¹¹ in copper containing approximately 2 per cent Ni and 0.1 per cent O_2 . Benard¹² has presented indirect evidence that 0.5 to 1.5 per cent Ni in anode copper may be oxidized during blowing and reduced to a substantial degree during poling. Little direct evidence exists of its behavior in the composition range under present consideration.

In the absence of oxygen, solid solubility is assured, and is reflected in the constancy of the conductivity data over the entire annealing range (Table 2). Very moderate losses of conductivity ensue, as illustrated by Fig. 2. The present data revise the effect of nickel downward by a small but definite amount, inasmuch as Skowronski and Archbutt and Prytherch¹¹ report a loss of conductivity of 4.6 per cent and about 5.2 per cent, respectively, for an addition of 0.05 per cent Ni, in contrast to the 4.1 per cent herein determined. When plotted on rectangular coordinates, a straight-line function may be obtained from 0 to 0.02 per cent Ni, and within this range the loss of conductivity is 0.09 per cent I.A.C.S. for each 0.001 per cent Ni by weight. Above 0.02 per cent, the unit effectiveness of nickel definitely decreases with increasing concentration.

The alterations in the annealing characteristics are of even lower order than the modest losses of conductivity. In fact, up to 0.05 per cent Ni, no significant change in softening temperature could be detected. Evidently, considerable quantities of nickel are necessary to raise the softening temper-

ature of pure copper to any appreciable degree.

The preparation of oxygen-bearing alloys was initially attempted by the diffusion

for ½ hr. at 600°C., and reduced 75 per cent to 0.081-in. test gauge. Oxygen contents were determined by loss in weight in hydrogen and are listed with the physical

TABLE 2.—Alloys of Nickel and Pure Copper

Sample No.	Ni, Per Cent	O ₂ , Per Cent	Hard Drawn	Conductivity, Per Cent I.A.C.S., Annealed at						Softening Temperature, Deg. C.
				300°C.	400°C.	500°C.	600°C.	700°C.	800°C.	
153M	Nil	Nil	100.3	102.25	102.25	102.25	102.25	102.3	102.3	146
154M	0.0007	Nil	100.2	102.1	102.1	102.1	102.2	102.15	102.2	140
155M	0.0015	Nil	100.0	101.95	101.95	102.0	102.0	102.1	102.15	138
156M	0.005	Nil	99.8	101.9	101.8	101.8	101.9	101.85	101.9	137
157M	0.01	Nil	99.35	101.3	101.4	101.4	101.45	101.5	101.4	139
158M	0.05	Nil	96.3	98.1	98.1	98.2	98.25	98.25	98.35	141
153MO ^a	Nil	0.019	100.25	102.2	102.3	102.25	102.3	102.25	102.35	142
154MO	0.0007	0.018	100.15	102.15	102.25	102.25	102.3	102.2	102.25	138
155MO	0.0015	0.015	100.1	102.0	102.0	102.15	102.2	102.1	102.2	140
156MO	0.005	0.017	99.8	101.7	101.85	101.8	101.9	101.85	101.85	140
157MO	0.010	0.016	98.8	101.3	101.4	101.3	101.3	101.45	101.35	145
158MO	0.050	0.017	96.4	98.2	98.2	98.4	98.3	98.3	98.25	144

^a Conductivity values of all oxygen-bearing samples were corrected for the volume effect of Cu₂O.

process employed for the iron series, but long periods at 850°C. did not produce a detectable change in the properties. Accordingly, larger amounts of oxygen were added by remelting suitable portions of the

data of Table 2. The incorporation of excess oxygen in the form Cu₂O displaces a certain volume of copper, and contributes to the conductivity loss in proportion to the volume of displacement. Corrections in the

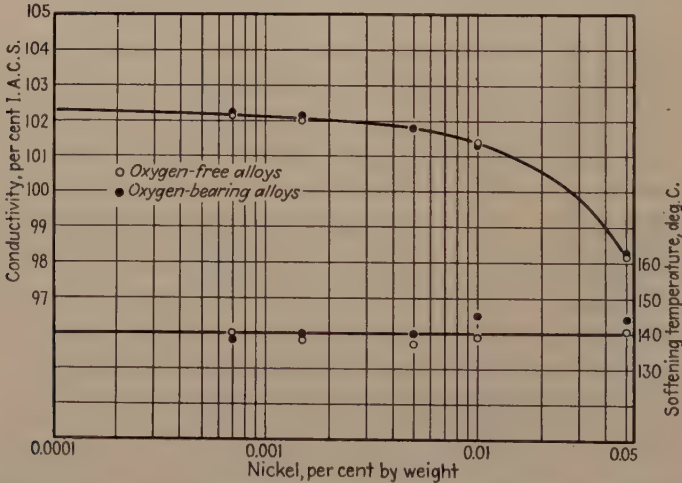


FIG. 2.—EFFECT OF NICKEL ON CONDUCTIVITY AND SOFTENING TEMPERATURE OF HIGH-PURITY COPPER.

alloys in a high-purity graphite crucible and casting through air. The 1-in. diameter billets produced were hot-rolled to 5⁄8-in. rod, cold-drawn to 0.162-in. wire, annealed

conductivity data have been made for this effect by adding 0.136 per cent I.A.C.S. to the measured conductivity values for each 0.01 per cent O₂ present.

Despite the presence of excess oxygen over the combining ratio, no evidence exists to suggest any appreciable formation of NiO in these alloys; the oxygen-free and oxygen-bearing data are identical for all practical purposes. These results are not incompatible with the evidence that NiO may form in the higher percentage range, for in all probability the reaction is reversible:



Higher amounts of either nickel or oxygen undoubtedly favor the formation of the oxide, and this view is particularly substantiated by the reversible behavior of the high-nickel anodes described by Benard. Rhines obtained divergent results from two alloys containing 0.11 per cent Ni oxidized by diffusion at 1000°C. where the solubility of oxygen¹³ approximates 0.0045 per cent, but concluded that a substantial amount of NiO was formed. The master alloy of the present series, containing 0.19 per cent Ni, was exposed to the diffusion process at 850°C. for comparison. The samples consisted of suitable portions of 1/4-in. rod cold-drawn from 3/8 in. After withdrawal from the furnace, the specimens were drawn to 0.081 in. and annealed at 500°C., and conductivity values were obtained. The progress of the reaction is indicated by the following data:

TIME OF DIFFUSION AT 850°C., HOURS	CONDUCTIVITY 0.19 PER CENT NI-PURE CU, PER CENT I.A.C.S.
0	87.7
48	91.6
96	92.4
168	92.8

It is apparent that the reaction of nickel with oxygen under these conditions is very slowly approaching an equilibrium value, which permits the presence of considerable amounts of soluble nickel. After 168 hr. at 850°C., approximately 0.06 per cent Ni has been precipitated as an oxide, leaving 0.13 per cent Ni in solid solution.

When remelted in a covered graphite crucible and poured through air, by the

procedure used to prepare the oxygen-bearing alloys more dilute in nickel, a casting containing considerably more oxygen was produced; the amount found by chemical analysis was 0.027 per cent O₂. However, the conductivity as measured on fabricated and annealed wire was found to be only 90.05 per cent (corrected for the presence of excess Cu₂O). Inasmuch as the melt was enclosed in a covered graphite crucible under highly reducing conditions, and was exposed to oxidation for only the relatively short time required for casting and solidification, it is obvious that the conditions favorable to the formation of nickel oxide were maintained for only a fraction of the time necessary for equilibrium to be reached. The importance of the time factor in the precipitation of small amounts of nickel, in the form of oxide, accounts for the difficulty in following the reaction by optical methods. The sharp boundary of the advancing zone of oxidation, so common to many copper alloys, is not present in this case where precipitation occurs in a more general manner.

Apparently, the characteristics of the reaction of nickel with oxygen indicate that the small amounts of this element found as an impurity in tough-pitch coppers may be present in soluble form. Fortunately, the amount required for appreciable effect on the conductivity and the softening temperature appears to be large.

EFFECT OF COBALT

Although rarely found in commercial electrolytic coppers, the effects of small additions of cobalt have been included in several of the earlier investigations. The present survey was abbreviated to the minimum required to ascertain its general behavior. This markedly resembles that of iron.

In the oxygen-free condition, complete solid solubility of cobalt is indicated and is accompanied by a substantial loss of con-

ductivity and a definite but small increase in softening temperature. Oxidation by diffusion at 850°C. proceeded rapidly in the 0.05 per cent Co alloy; as illustrated by Table 3, it approaches complete rejection of cobalt from solid solution as an oxide, making appropriate allowance for its volume effect. By way of exception to the general rule, the softening temperature of this sample was in no way diminished by the oxidation, but additional evidence would be required to prove the generality of this behavior, inasmuch as the particular

Hume-Rothery,¹⁵ this constitutes a valency effect.

To the left of copper in the first long period, the transitional elements, nickel, cobalt and iron, present atomic structural differences associated with an inner electron shell, and the previously determined data have not lent themselves to expression in terms of a simple ratio. From the present data covering the very dilute alloys, where the lowering of conductivity per unit of solute is a maximum, and is practically constant for a limited composition range,

TABLE 3.—*Alloys of Cobalt and Pure Copper*

Sample No.	Co, Per Cent	O ₂ , Per Cent	Hard Drawn	Conductivity, Per Cent I.A.C.S., Annealed at						Softening Temperature, Deg. C.
				300°C.	400°C.	500°C.	600°C.	700°C.	800°C.	
261M	Nil	Nil	100.3	102.2	102.25	102.3	102.3	102.25	102.2	135
292M	0.002	Nil	99.2	101.35	101.4	101.4	101.4	101.25	101.3	145
293M	0.01	Nil	96.2	98.1	98.2	98.15	98.3	98.1	98.15	163
294M	0.05	Nil	83.3	85.45	85.0	85.0	84.9	84.8	84.8	160
294MO	0.05	S ^a		101.65	101.7	101.75	101.9	101.9	101.65	166

^a Saturated with oxygen by diffusion at 850°C.

form and dispersion of the oxide formed under these conditions may have been responsible for the anomaly.

PERIODIC RELATIONS

The magnitude of the effect of many solute elements on the resistivity of a number of solvent metals, including copper, was demonstrated by Norbury¹⁴ to be closely related to the respective positions occupied by the foreign and host metals in the periodic table. Linde has shown that the increase in resistivity of copper alloys per unit atomic per cent of the addition metal, plotted against $(n - n')^2$, where n and n' are the atomic numbers of the solute metal and of copper, respectively, results in a straight line for those elements to the right of copper in the first long period. In these cases the atomic structure of each solute element differs from its neighbor by reason of the addition of one electron to the outer shell, and, as pointed out by

the increase in resistivity per 0.01 atomic per cent of each element may be determined as follows:

SOLUTE ELEMENT, ATOMIC PER CENT	INCREASE IN RESISTIVITY OHMS PER METER-GRAM $\times 10^3$
0.01 Ni	1.18
0.01 Co	5.78
0.01 Fe	10.67

Although the increases in resistivity are not related according to the 1:4:9 ratio corresponding to $(n - n')^2$, their effects may be expressed in terms of a whole number relationship according to the ratio 1:5:9. While the existence of a simple function between the conductivity effects of these elements and the differences in the number of electrons between the solute and solvent metals is more closely demonstrated by the present data than heretofore, the results obtained for cobalt complicate the relationship. A rather small degree of contamination of the cobalt alloys by an extraneous element having a large effect on conductivity, such as iron, could readily

account for the deviation. However, spectrographic analysis of all the cobalt-copper alloys is in complete disagreement with this possibility, since nothing but copper and

oxygen is reversible, and the amount of nickel oxide formed depends on the concentration of the reactants and the time at the reaction temperature. It is quite

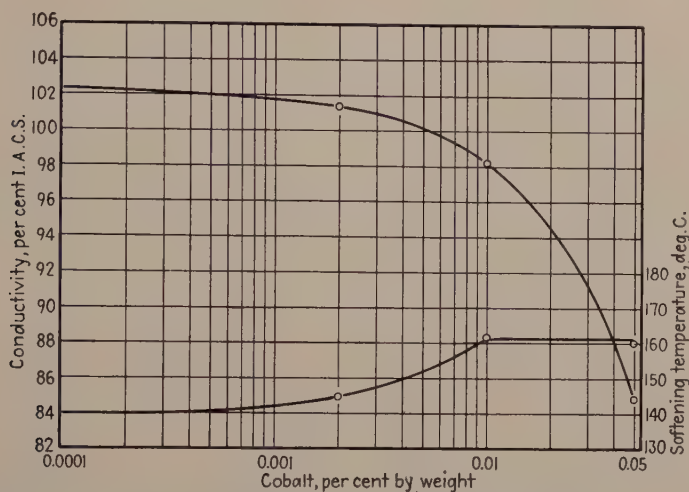


FIG. 3.—EFFECT OF COBALT ON CONDUCTIVITY AND SOFTENING TEMPERATURE OF OXYGEN-FREE HIGH-PURITY COPPER.

cobalt could be detected in these, or in the master alloy containing 0.2 per cent Co used to compound the series.

SUMMARY

1. Iron forms a limited series of solid solutions with oxygen-free copper and reduces its conductivity to a marked degree. From 0 to 0.005 per cent Fe, the loss of conductivity amounts to 0.80 per cent I.A.C.S. for each 0.001 per cent Fe by weight. In amounts up to 0.05 per cent Fe, the effect of iron on the softening temperature is very small. The reaction between oxygen and iron to form Fe_3O_4 is quantitative. Consequently, the iron content of tough-pitch coppers is present only as an inert oxide.

2. Nickel has a comparatively small effect on the conductivity of oxygen-free copper (0.09 per cent per 0.001 per cent Ni) and, up to 0.05 per cent Ni, no detectable increase in softening temperature was observed. The reaction of nickel with

possible that the reaction proceeds to an appreciable extent only in the presence of considerably more nickel and oxygen than is present in commercial electrolytic coppers.

3. Cobalt enters solid solution in oxygen-free copper and is responsible for a sizable decrease in conductivity (0.43 per cent per 0.001 per cent Co). Up to 0.05 per cent, cobalt has but a minor effect on softening temperature. Oxygen completely precipitates cobalt as an oxide.

4. Nickel, cobalt and iron behave similarly with respect to softening temperature, but their relative effects on resistivity increase in the direction of their displacement from copper in the periodic system by the whole number ratio 1:5:9.

ACKNOWLEDGMENT

The authors are particularly indebted to Dr. A. J. Phillips, under whose direction the present research program is being conducted, for his counsel and guidance.

Mr. Stephen Mikula has rendered painstaking assistance in preparing and testing many of the samples. Thanks are also due the American Smelting and Refining Co. for permission to publish the results.

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DISCUSSION

(S. Skowronski presiding)

H. E. STAUSS,* Newark, N. J.—This paper is very interesting to one working with platinum because his problems are related to some of the problems of high-purity copper. One fact that strikes me is that no use is made in this work of the thermal electromotive force for comparing the amounts of minute impurities. Fig. 1, showing that the effect of iron on copper can be removed by oxidation, is interesting, because platinum too can be apparently improved in purity by heating in oxygen at high temperatures, to judge from physical properties alone. The question arises in certain instances of how to define purity when dealing with the physical properties of metals—whether in terms of chemical purity or of the amount of foreign elements in solid solution, ignoring inclusions.

It is interesting that some elements produce relatively small, continuous effects upon the softening temperature of copper. General experience with platinum had led me to assume that the hardening effect of impurities took a rather discontinuous jump when enough

impurity was added, somewhat like the curve shown for cobalt.

J. S. SMART, JR. (author's reply).—Mr. Stauss has raised several interesting points, which have considerable bearing on the interpretation to be placed on the data presented in this paper. The oxidation of certain soluble impurities can be carried out in many solvent metals, and copper and platinum are but two examples of a rather large group.

Unfortunately, the purity of most metals, as commercially marketed, cannot be defined by the simple expedient of considering all the soluble impurities as "actives" and the oxidized impurities as "inactive inclusions." The effect of the soluble impurity under consideration upon the physical property in question depends to a very great degree upon its concentration. In some cases a minute amount of soluble impurity may have a large effect; in others, a considerable initial addition may have a negligible influence, which may or may not vary as the concentration is increased. Furthermore, dispersed oxides cannot be dismissed as inactive with respect to all physical properties, as illustrated by their well-known tendency to restrict grain growth, and so forth.

Obviously, the true picture can be obtained only by a comprehensive study of the detailed behavior of the various impurities. In this connection, it is both convenient and practical to employ methods that yield data of commercial significance, and for copper, conductivity and softening temperature are to be preferred to thermal electromotive force.

We are in complete agreement with Mr. Stauss that the effect of impurities on the softening temperature is discontinuous. In every case studied we have observed an initial concentration zone in which the effect is relatively small and continuous, followed by a zone of much greater effect, after which the influence becomes small again, and sometimes negligible. An important feature of this behavior is the fact that the concentration zone of high effectiveness is different for each impurity. In iron, the jump in the curve occurs beyond 0.05 per cent Fe, and Fig. 1 lies wholly within the initial continuous portion. This explains why previous observations on the high effectiveness of iron obtained from more concentrated alloys do not apply to its behavior in coppers of commercial purity.

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Structure of Copper after Rolling

BY CHARLES S. BARRETT,* MEMBER A.I.M.E., AND F. W. STEADMAN†

(New York Meeting, February 1942)

DEFORMATION bands of surprising regularity are found in large-grained polycrystalline copper after cold-rolling (Fig. 1). Individual bands frequently are large enough to permit a determination of their orientation by means of etch pits and an optical goniometer. Measurements have been made on 21 areas in seven different grains, and these, combined with X-ray studies of nine single crystals that had been cold-rolled after mounting in a polycrystalline block, have contributed to a better understanding of the preferred orientations in rolled copper just as similar studies have for rolled iron¹ and brass.^{2,3} Particular attention was given to determining orientations that are stable during rolling and to the manner of fragmentation and rotation of unstable grains. The possible role of twinning was also carefully investigated.

The texture of polycrystalline copper after cold-rolling is well established by the pole figures that have been plotted by Schmid and Staffelbach,⁴ Iweronowa and Schdanow,⁵ and Brick and Williamson,³ all of which are in substantial agreement. There has been some divergence in the list of individual "ideal" orientations that have been used to describe the texture by these observers and others,⁶ although the orientation (110) $[\bar{1}12]$ —that is, (110) parallel to the rolling plane and $[\bar{1}12]$ parallel to the rolling direction—is generally recognized as

the most prominent orientation and (112) $[\bar{1}1\bar{1}]$ one of the lesser orientations. Other orientations have been given by some observers as (236) $[53\bar{3}]$, (100) $[001]$, and (110) $[001]$. The texture of copper has also been described as (135) $[53\bar{3}]$.^{6,7} The sum of these orientations provides a reasonable approximation to the complete pole figure, but it does not follow that these specific orientations are necessarily of fundamental significance, for the choice of indices is arbitrary, within limits. Furthermore, a detailed investigation of the ideal orientations in cold-rolled iron discloses continuous ranges of equally favored positions rather than definite positions of high stability,¹ and similarly Brick's observations in a single crystal of α brass² suggest that all orientations in the range between (110) $[\bar{1}13]$ and (110) $[\bar{1}17]$ are about equally stable.

MATERIALS AND METHODS

The material used was vacuum-cast electrolytic copper kindly supplied by L. L. Wyman, of the General Electric Co.* Slices $\frac{1}{2}$ in. thick and $2\frac{1}{2}$ in. square, cut from the ingot, were rolled with 50 per cent reduction per pass to final thicknesses between 0.02 and 0.04 in., and etched to develop cube-face etch pits suitable for goniometric work.⁸ The etch was light on some strips and deep in others.

* Manuscript received at the office of the Institute Dec. 1, 1941. Issued as T.P. 1430 in METALS TECHNOLOGY, February 1942.

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¹ References are at the end of the paper.

* Mr. Wyman stated that he was somewhat uncertain of the purity as the ingot was prepared years ago under "not too good vacuum conditions." The rolling texture and recrystallization textures, however, are not sensitive to oxygen content.⁷

Individual crystals about 0.3 in. on an edge were cut out and mounted in tight-fitting holes in copper blocks of the same thickness (Fig. 2). These were rolled to 80 or 90 per cent reduction in 30 to 40 passes



FIG. 1.—TYPICAL DEFORMATION BANDS IN LARGE GRAINS OF ROLLED COPPER. $\times 2$.

Etched in solution of hydrochloric acid and ferric chloride.

and a representative portion of each was removed for study, while other portions were again carefully fitted into a plate for additional rolling to a total reduction of 96 or 98 per cent. Rolling was continued until each crystal fell out of its holder. The rolled pieces were thinned by etching to approximately 0.004 in. for X-ray transmission patterns (molybdenum radiation). Orientations were determined by pole figures, and when the range in orientation was not large the results were checked by the optical goniometer.

RESULTS

Crystals having specially chosen orientations were rolled to see whether these orientations were truly stable. The initial orientations of the crystals with respect to the rolling plane and rolling direction are listed below, together with a brief summary of the results.

(110) $[\bar{1}12]$.—A crystal starting with this important orientation exhibited only a slight rotation during rolling, indicating that this orientation is more stable than any of the others listed below. After a 55

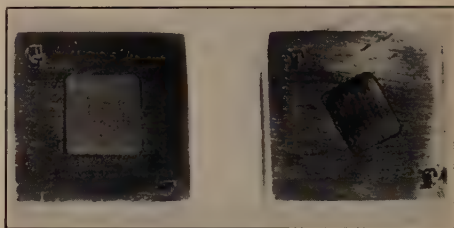


FIG. 2.—COPPER SINGLE CRYSTALS MOUNTED IN POLYCRYSTALLINE COPPER BLOCKS FOR ROLLING IN CHOSEN DIRECTIONS. $\times 1$.

per cent reduction there was no rotation, and after a 97.6 per cent reduction (41 passes) there was a rotation of only 10° (about an axis that was inclined to all axes of symmetry of the rolling process and of the initial crystal). The final orientation was remarkably sharp, with a range of about $\pm 5^\circ$ around the sheet normal and $\pm 10^\circ$ around axes in the plane of the sheet. No secondary orientations were found with the optical goniometer or with X-ray diffraction. It is concluded that a copper crystal with an orientation in the vicinity of (110) $[\bar{1}12]$ resists rotation and fragmentation into bands much as a crystal of aluminum does when compressed on a plane near (110).⁹

(110) $[001]$.—A specimen was cut from the preceding one after 55 per cent reduction (which left it a pseudo single crystal) and inserted in a block so as to be rolled in the direction of the cube axis; i.e., with the initial orientation (110) $[001]$. The reduction in this second block was 83 per cent. Lattice rotation occurred, chiefly around the sheet normal, in both directions from the initial $[001]$ position. Fragments were distributed, in decreasing numbers, from the initial orientation to positions 25° from this; the total range of scattering included the positions (110) $[001]$, (110) $[\bar{1}17]$,

(110) $[\bar{1}15]$ and (110) $[\bar{1}13]$. Judging from other crystals, further rolling might have extended this spread to (110) $[\bar{1}12]$ and perhaps ultimately concentrated the fragments at this position.

(112) $[\bar{1}1\bar{1}]$.—After 86 per cent reduction an optical goniometer study of this crystal indicated that the rolling plane had rotated only 6° from (112) and the rolling direction had moved 8° from $[\bar{1}1\bar{1}]$. After 96 per cent

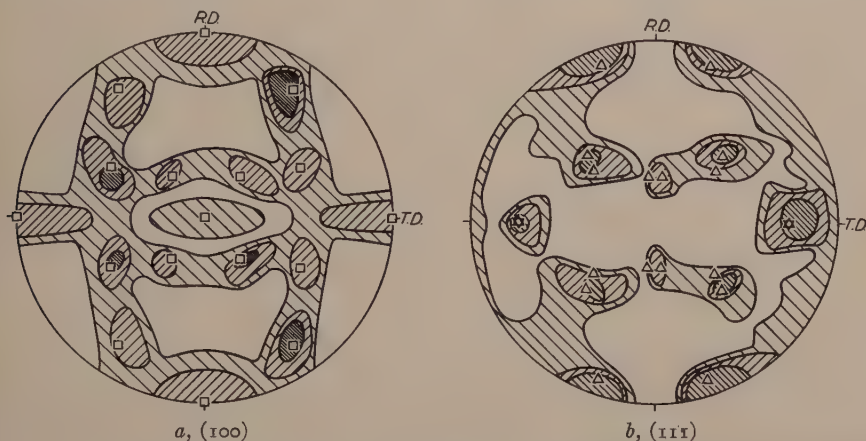


FIG. 3.—POLE FIGURES FOR CRYSTAL ROLLED ALONG (100) $[001]$ TO REDUCTION OF 98.1 PER CENT. Orientations indicated are complementary $(135) [2\bar{1}\bar{1}]$ and (100) $[001]$.

A wide range of orientations around the sheet normal like this has been observed in a rolled brass crystal (a crystal initially near (110) $[001]$, (Fig. 7 of ref. 2) and doubtless contributes to the wide azimuthal spread in corresponding portions of the polycrystalline pole figure of copper and brass.

(110) $[\bar{1}15]$.—A section cut from the pseudo single crystal having the orientation (110) $[\bar{1}12]$ after 55 per cent reduction was inserted in a block so as to be rolled along (110) $[\bar{1}15]$ and was reduced 73 per cent in this block. The crystal remained a pseudo single crystal and rotated to the position (110) $[\bar{1}12]$. The spread was as small as in the crystal that started in the (110) $[\bar{1}12]$ position, and no minor orientations appeared.

From these first three crystals it appears that (110) $[\bar{1}12]$ is approached by rolling in any direction in the (110) plane, but with ordinary degrees of reduction it may not be possible for all fragments to rotate far enough to reach this end position.

reduction it was found by X-ray pole figures that strong symmetrical ("complementary") (112) $[\bar{1}1\bar{1}]$ orientations had developed. While there was negligible azimuthal spread in orientation around the sheet normal, there was a large spread around the transverse direction in the sheet ($\pm 50^\circ$ to 80°), within which was the position (110) $[001]$.

A similar large spread around the transverse direction has been noted in a brass crystal (Fig. 5a, ref. 3) with an initial orientation (111) $[\bar{1}1\bar{2}]$, after 80 per cent reduction.

(100) $[001]$.—This crystal, when rolled 98.1 per cent, developed virtually the entire polycrystalline texture, as will be seen from the cube and octahedral pole figures of Figs. 3a and 3b, prepared from several dozen X-ray films. It is interesting that the intensity maxima on these pole figures are sharp and enable indices to be assigned more definitely than can be done on the usual polycrystalline plots. The best fit seems to lie very close (within experi-

mental error) to the orientation $(113) [21\bar{1}]$. All four complementary orientations of this type are well represented, but two are slightly stronger than the others.*

$(113) [\bar{1}10]$ crystal, except that they were mirror images of the preceding crystal in the plane normal to the rolling direction. The resemblance was striking, for each

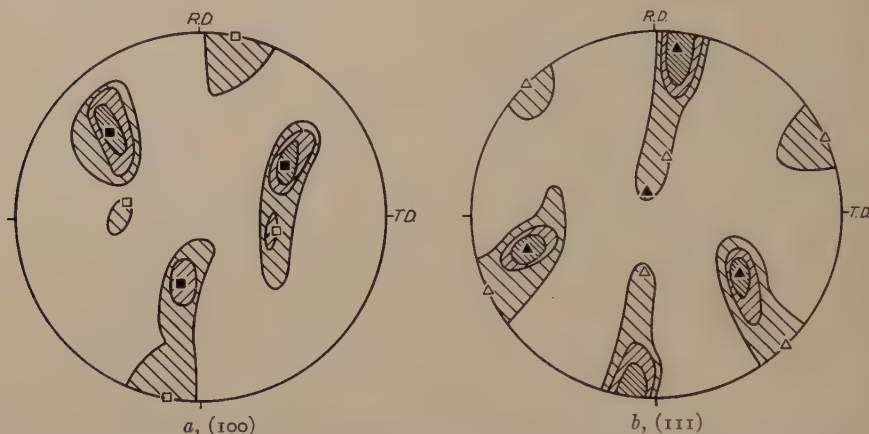


FIG. 4.—POLE FIGURES FOR CRYSTAL ROLLED ALONG $(113) [\bar{1}10]$.

Filled squares and triangles represent the orientation $(234) [32\bar{3}]$; open ones, the minor orientation $(110) [\bar{1}17]$, which is not a twin of the dominant orientation.

$(113) [\bar{1}\bar{1}0]$.—After rolling 97.5 per cent, this crystal had orientations represented by the pole figures of Figs. 4a and 4b. The orientation spreads chiefly around the transverse direction, as in the $(112) [\bar{1}1\bar{1}]$ crystal. The dominant orientation has (112) within 10° of the rolling plane and $[\bar{1}1\bar{1}]$ about 10° from the rolling direction; it could be assigned indices $(234) [32\bar{3}]$. The scatter includes the orientation $(110) [\bar{1}17]$, which has been indicated in Fig. 4 as a minor orientation. This minor orientation is not a twin of the major orientation.

$(120) [\bar{2}11]$.—Although this initial orientation was quite different from the preceding one, the orientations after 96 per cent reduction were very similar; the resulting orientations closely matched those of the

X-ray exposure of this crystal was a mirror image of the corresponding film for the preceding crystal.

$(112) [\bar{1}10]$.—Each X-ray film of this crystal could be matched by superimposing the corresponding films for the two preceding crystals. The texture (with 98 per cent reduction) thus was symmetrical with respect to the plane normal to the rolling direction, and could be described as two complementary dominant orientations $(234) [32\bar{3}]$ and two complementary minor orientations $(110) [\bar{1}17]$, which are shown stereographically in Fig. 5.

An optical study of this crystal after a preliminary rolling of 92 per cent revealed two orientations near $(112) [\bar{1}1\bar{1}]$, which were approximately mirror images of each other and were close to the major orientations that were found after 98 per cent reduction. This indicates that the major portion of the material is stable in orientations near $(112) [\bar{1}1\bar{1}]$. (This is in accord with results for the $(112) [\bar{1}1\bar{1}]$ crystal; the pole figures for these two crystals are

* Indices $(135) [53\bar{3}]$, which sometimes have been used for the polycrystalline texture, do not seem to fit as well, and furthermore are not self-consistent ($1 \times 5 + 3 \times 3 - 5 \times 3 \neq 0$). Indices $(358) [58\bar{3}]$ would serve well, but are less likely to be significant and are not self-consistent.

similar, with spreads chiefly around T.D. as an axis.)

Search for Twin Orientations.—The two symmetrical (110) $[\bar{1}12]$ orientations that predominate in polycrystalline copper have been attributed by Cook and Richards¹⁰ to twinning during rolling. While it is true that they stand in twin relation to each other, it should be noted that this may simply result from the symmetry of the rolling process and not from a twinning mechanism. (Two other possible twin orientations are *not* observed.) Brick and his co-workers have considered deformation twinning as likely in copper and brass, but have found no conclusive proof of it. Since twinning would be an important factor in theories of recrystallization textures as well as deformation textures, a careful search was made for twin orientations in X-ray films of crystals, with the results shown in the accompanying table.

Search for Twins in X-ray Films

- (110) $[112]$, reduced 97.6 per cent: single orientation—no twins
- (110) $[001]$, reduced 83 per cent: large scatter around one orientation—no twins
- (110) $[\bar{1}15]$, reduced 73 per cent: single orientation—no twins
- (112) $[11\bar{1}]$, reduced 96 per cent: complementary orientation is same as a twin—ambiguous
- (100) $[001]$, reduced 98.1 per cent: polycrystalline texture—ambiguous
- (113) $[\bar{1}10]$, reduced 97.5 per cent: major and minor orientations that are not twins
- (120) $[\bar{2}11]$, reduced 96 per cent: major and minor orientations that are not twins
- (112) $[\bar{1}10]$, reduced 98 per cent: two major and two minor orientations, not twins

It is evident that these experiments give no indication of twinning during de-

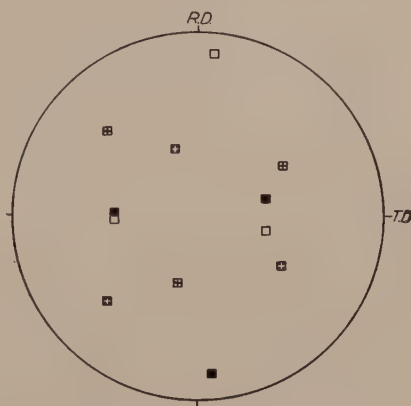


FIG. 5.—CUBE POLE FIGURE OF MEAN ORIENTATIONS IN CRYSTAL ROLLED ALONG (112) $[\bar{1}10]$. Dominant orientations (white and black crosses) are complementary (234) $[32\bar{3}]$; minor orientations (open and filled squares) are complementary (110) $[\bar{1}17]$ (approximately).

An exhaustive search for twins was carried out in a crystal that had been reduced only 31 per cent and that had retained a very sharp single orientation (135) $[21\bar{1}]$. A stereographic plot of the orientation was prepared, and the strongly reflecting planes of all twins were also located on the plot. A strip of the deformed crystal was then X-rayed at various angles chosen to bring out reflections from each of the possible twins. However, only the single orientation was found even with very heavy exposures; it was concluded that none of the possible first-order twins could be present in greater volume than $1/14,000$ of the volume of the crystal.

formation at either intermediate or high reductions.

Polycrystalline Strips.—Three strips of large-grained copper rolled 92 to 96 per cent were cut into small segments and studied on the optical goniometer. While the measurements were unsuited to detecting minor orientations, they showed nicely the relation between the orientations in adjoining bands. Nearly all grains contained bands of some sort (see Fig. 1), some straight, some irregular, some extending across the entire grain and some running in but a short distance from a boundary. Usually the bands that extended almost longitudinally in the strip were the straight-

est and narrowest. In many cases the principal orientations in adjacent bands of a crystal were approximately mirror images of each other in the planes of symmetry of

Twenty-one orientations were measured on seven different crystals. The (111), (100) and (110) pole figures constructed from these are in satisfactory agreement with the

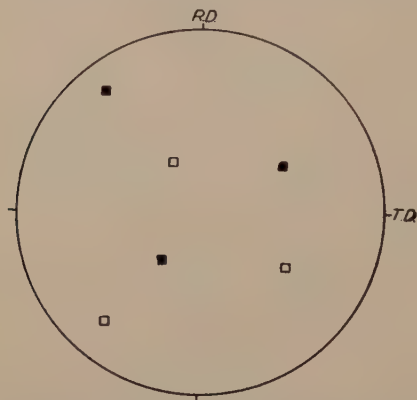


FIG. 6a.—CUBE POLE FIGURE OF MEAN ORIENTATIONS IN DEFORMATION BAND AND ADJOINING MATRIX.

Deformation band, represented by hollow squares, shows mirror relation to the matrix (solid squares).

the deformation. In others they were mirror images in some other plane containing the normal direction. Typical orientations are

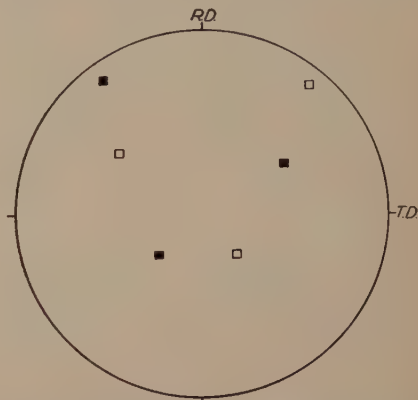


FIG. 6b.—ORIENTATION OF DIFFERENT BANDS (OPEN SQUARES) IN SAME CRYSTAL (FILLED SQUARES).

pole figures for polycrystalline copper, and also are in agreement with the combined pole figures for the single crystals that were discussed in the first part of this paper. Combined pole figures for mean orientations

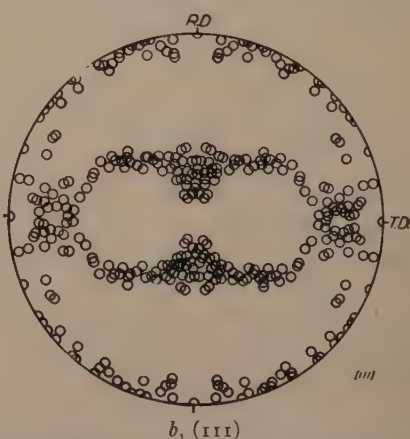
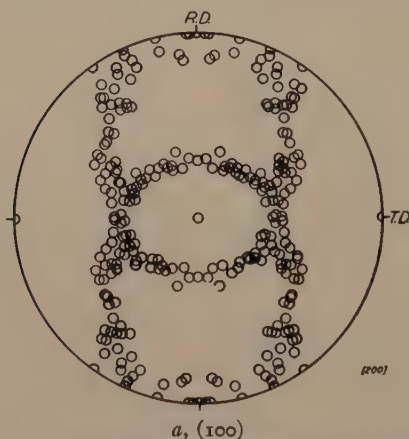


FIG. 7.—COMPOSITE POLE FIGURES OF ALL MEAN ORIENTATIONS IN INDIVIDUAL AREAS OF ROLLED COPPER CRYSTALS AND GRAINS.

Consistent with polycrystalline pole figures.

plotted in Fig. 6; Fig. 6a is a mirror relation with respect to the N.D.-T.D. plane and Fig. 6b is a mirror relation with respect to the N.D.-R.D. plane. Neither of the sets shows a twin relationship.

in all areas studied by X-rays and optical goniometer are reproduced in Fig. 7. The general outlines resemble the published pole figures for polycrystalline material and indicate that the methods employed in

this study satisfactorily reproduce polycrystalline conditions.

SUMMARY AND CONCLUSIONS

1. Preferred orientations in rolled copper have been investigated using large-grained material and single crystals mounted in polycrystalline blocks.

2. Multiple orientations develop in nearly every grain. Grains with a (110) rolling plane and a $[112]$ rolling direction are exceptions; two crystals had this single orientation even after 97.6 per cent reduction in thickness.

3. All ideal orientations that have been listed for rolled copper except $(110)[112]$ are unstable; if a grain starts in one of these orientations it will rotate into one or more new orientations. The entire polycrystalline texture developed in a crystal that was initially $(100)[001]$, and a wide spread around the transverse direction in the sheet developed in several, including one that was initially $(112)[11\bar{1}]$. Pole figures for these are presented.

4. The principal orientations in polycrystalline copper can be given the indices $(234)[32\bar{3}]$ or $(135)[21\bar{1}]$.

5. Deformation bands that appear when large-grained rolled copper is etched consist of adjoining regions having orientations that usually are mirror images of each other, the mirror planes being symmetry planes for flow during rolling.

6. The multiple orientations in individual crystals were searched for relations that could be explained by deformation twins but no evidence of twinning was found. While symmetrical $(110)[112]$ positions happen to be in twin relation (Cook and Richards¹⁰) this apparently is coincidental.

ACKNOWLEDGMENT

The authors acknowledge the able assistance of L. H. Levenson, formerly Research Assistant in the Metals Research

Laboratory, in the early stages of this work.

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DISCUSSION

(L. S. Fletcher presiding)

W. M. BALDWIN, JR.,* Cleveland, Ohio.—In 1936 Bryukhanov,¹¹ using elasticity data, demonstrated that the rolling texture of copper could not possibly be the $(110)[112]$ orientation but that the $(135)[21\bar{1}]$ (or possibly the $(124)[21\bar{1}]$) orientation fitted his data nicely. This substantiates Dr. Barrett's conclusion 4. With two such different experimental methods pointing to the same conclusion, it would seem that there is a strong case for the $(135)[21\bar{1}]$ orientation being the copper-rolling texture.

On the other hand, Dr. Barrett finds that the $(135)[21\bar{1}]$ orientation is unstable when it is cold-rolled from a soft condition. These two facts are not, I think, incompatible. It is entirely possible that there are differences between a given orientation in the hard-rolled condition and the same orientation in the soft condition. We know definitely that there are differences in a given orientation in hard-rolled metal when the hard-rolled metal has been produced in different ways. In rolled copper, for instance, the orientation, $(110)[112]$, may be eradicated or retained by the annealing process, dependent upon the rolling schedule.¹² We know so little concerning the internal structures of metals that it would be foolish to set up any theories here; but it would not be too much to say that these two facts concerning the $(135)[21\bar{1}]$ orientation are not contradictory.

* Research Department, Chase Brass and Copper Co.

¹¹ Bryukhanov: *Tech. Phys. of the U.S.S.R.* (1937)

4, 1027.

¹² W. M. Baldwin, Jr.: *A.I.M.E. Tech. Pub.* 1455 (*Metals Tech.*, June 1942).

Last May, Vacher¹³ conducted a work similar to Dr. Barrett's; i.e., he rolled down a number of single crystals, tracing the progressive orientational change at intervals in the rolling

being two of the preferred orientations developed in copper strip is important as these orientations apparently are not developed in brass strip. This indicates that the development



FIG. 6.—COMPARISON OF RESULTS.

Broken lines: Octahedral pole figure of (001) 100 single crystal rolled 98.1 per cent (Barrett).

Solid lines: Octahedral diffraction arcs from a near (001) 100 single crystal rolled 99 per cent (Vacher).

process. Fig. 6 shows how well their results coincide for the one orientation that is common to both papers: (001) [100]. This coincidence is exceedingly good in view of the fact that in rolling single crystals there is not the advantage of a statistical average, as in rolling polycrystalline strip.

H. C. VACHER,* Washington, D. C.—Some recent work,¹³ not reviewed by the authors, deserves mention, especially since the results are in good agreement with those presented by the authors. It is noteworthy that in both investigations complementary (112) [11 $\bar{1}$] orientations were found after monocrystalline specimens, having different initial orientations, had been cold-rolled severely, thereby indicating a high degree of stability for this combination of orientations. The establishment of complementary (112) [111] orientations as

of cold-rolled textures in copper and brass strips cannot be explained entirely by slip on octahedral planes in dodecahedral directions. Interesting results should be obtained from a detailed study of the changes in metallographic and X-ray structures resulting from cold-rolling large monocrystalline specimens of copper and brass having initially the (112) [111] orientation.

The authors showed that after considerable reduction a monocrystalline specimen initially having the (110) [112] orientation did not develop the complementary orientation. Is it possible that in the preparation of specimens for X-ray analysis sufficient metal was dissolved to remove layers having the complementary orientation? In the work cited above, diffraction patterns of a monocrystalline specimen after 99.5 per cent reduction indicated two orientations in the top rolling plane and one in the bottom plane, the latter being the same as one of the orientations in the top plane.

* National Bureau of Standards.

¹³ Vacher; *Jnl. of Res., Nat. Bur. Stds.* (1941) 26, 385-404; RP 1385.

R. M. BRICK,* New Haven, Conn.—The authors do metallurgy a good service in demonstrating the inadequacy of many theories that have been presented here and in other journals; for example, proposals that a “new” type of solid solution occurs in aluminum-silver alloys; that the fragmentation accompanying fatigue stresses is useful in predicting when failure is imminent; that roller fragments between glide lamellae are the nuclei for recrystallization, and others.

This particular paper, in addition to showing the manner in which deformation textures originate in copper, presents some very interesting evidence on the question as to whether there are or are not mechanical twins in the deformed lattice.

The statement that twinned orientations, if present, occur in a proportion of less than one part in 14,000 is, as would be expected from these authors, a conservative factual statement based on unquestionable experimental data. In view of the manner in which it was made, it need not be pointed out that it does not eliminate the possibility of the existence of mechanical twins in the deformed structure.

For years, no evidence of precipitation in some aged, supersaturated solid solutions was detectable because X-ray diffraction studies did not reveal any lattice changes or any new lattice present in the solid solution. This fact deserves emphasis here, since it is now known, partly through Dr. Barrett's work in age-hardening, that there are precipitated platelets, not readily detectable by X-rays, of a transitional phase along the Guinier-Preston zones of the matrix lattice. I do not know what proportion of the total volume may be represented by these platelets; it would vary in different alloys and may be considerably more than one part in 14,000. At any rate, the X-ray evidence presented by the authors in regard to twins does not prove there are no mechanical twins present nor that an amount of less than one part in 14,000 may not determine the recrystallization texture.

Annealed brass or copper shows twins in the recrystallized structure. What is their origin? Did they originate during the recrystallization process or during the prior deformation? They are present when the recrystallization nuclei

or new grains first become visible under the microscope. It has seemed to me that they could have originated in the deformation process, occupying the octahedral plane which is the potential twinning plane and also the deformation plane of brass and copper.

The authors speak in their paper of deformation bands. I should like to emphasize that these are not identical to strain markings. Deformation bands are of an appreciable width and there is no doubt, from the authors' work, that these originate by rotation of different parts of the crystal in different directions. Within the bands, there are very thin etch markings, which have been analyzed, in many cases, and found to delineate octahedral planes. It is these line markings that may be mechanical twins, and which Dr. Barrett and Mr. Steadman have shown, if they are mechanical twins, are present in a volume of less than one part in 14,000.

I should be interested in knowing whether, subsequent to the work published in this paper, any of these deformed structures have been recrystallized and, if so, whether any correlation has been found between the deformation textures shown here and the recrystallization textures. Finally, do the authors have a theory as to the origin of annealing twins, which, although lacking experimental support, might be suggestive of ideas as to the origin of recrystallization structures and textures?

C. S. BARRETT (author's reply).—Mr. Baldwin notes that the $(135)[21\bar{1}]$ orientation is not stable when soft copper is rolled, but apparently is stable in the hard-rolled sheet. We do not actually have data on a single crystal starting with this orientation, but somewhat similar orientations appear to be unstable. Perhaps, as Mr. Baldwin suggests, the strain-hardened and the annealed lattices react differently, but any quantitative theory of such an effect can scarcely be hoped for because of the great number of active slip planes during rolling.

Mr. Vacher's work, done independently and simultaneously with ours shows similar results in many instances. We diverge somewhat in interpretation, however. Mr. Vacher interprets many of his complementary orientations as “twins.” We believe that complementary $(110)[\bar{1}12]$ orientations have “twin” orientations only by coincidence. All “twins” we have found

* Hammond Laboratory, Yale University.

have complementary orientations and we have found several complements that are not twins. Thus we think the production of symmetrical orientations is through the formation of complementary deformation bands rather than twins.

We believe the term "twin" should not be used unless it is meant that a region assumes its orientation by a true twinning process; progressive rotation of deformation bands into complementary orientations does not constitute a twinning process.

While it is possible to describe the polycrystalline pole figure approximately as twin $(110) [\bar{1}12]$ and twin $(112) [11\bar{1}]$ orientations, as Mr. Vacher does, other ideal orientations can also be used. Mr. Vacher's pole figures for individual crystals are scarcely detailed enough to indicate one ideal orientation in preference to another, and we do not see that they confirm twinning as against complementary orientations (see, for example, the arcs of Fig. 6, of Mr. Baldwin's discussion), or that they necessarily lead to the conclusion that complementary $(110) [\bar{1}12]$ and $(112) [11\bar{1}]$ orientations are the true end points of the rolling process.

In reply to the second paragraph of Mr. Vacher's discussion, we note that our (110)

$[\bar{1}12]$ crystal developed no complementary orientations that could be detected on X-ray films after etching to $\frac{5}{8}$ of the original thickness. However, there were some bands visible on one surface of the etched piece, covering a portion of that surface, which may have indicated a trace of material in complementary orientations. With deformations in general, complementary orientations are not developed in a crystal having an initial orientation that is a principal orientation of the final texture.

Dr. Brick correctly points out that deformation twins might be present in sufficient numbers to be important as recrystallization nuclei and yet not be seen on X-ray films. We readily admit this and have long been annoyed by the fact that the actual recrystallization nuclei can probably never be detected by X-rays, since they constitute such a small fraction of the total volume. To add to the difficulties, it may also be true that the dimensions of each of the twins, if they exist, are so small that only diffuse reflections could be obtained from large quantities of them. In this case the limiting ratio 1:14,000 for their volume would have to be lowered. We have made no recrystallization studies on these samples.

Strength Distribution in Sunk Brass Tubing

BY GEORGE SACHS,* MEMBER, GEORGE ESPEY* AND G. B. KASIK,* STUDENT ASSOCIATES A.I.M.E.

(Philadelphia Meeting, October 1941)

It has been reported frequently that the hardness and strength vary over the cross section of cold-worked, particularly cold-drawn, material. Brass rod and wire usually have been found to possess a maximum strength and hardness near the surface.^{1,2} According to Sachs,¹ the center fiber has about the same strength as a wire stretched by the same amount in a tensile-test machine, the strength increasing toward the surface (Fig. 1). These differences are particularly large for wire given a small reduction on drawing through a die with a wide opening. However, with increasing reduction and hardness, a tendency to form a thin soft surface skin becomes apparent. On the contrary, copper wire has usually been found to possess a soft surface skin³⁻⁵ and it has been reported by Harris³ that during the cold-drawing of hot-rolled wire the surface layer becomes increasingly softer than the core, while the layer of maximum strength moves toward the core, it being found near the surface at first.

The increase of strength and hardness from the core to the skin is readily explained by the observation that, in addition to the stretching, the layers of a rod or wire are sheared more the closer they are to the surface.^{1,6-8}

However, the presence of a soft surface layer can be attributed only to an annealing effect. The source of such a softening

might be the extremely high temperature that originates from the friction between

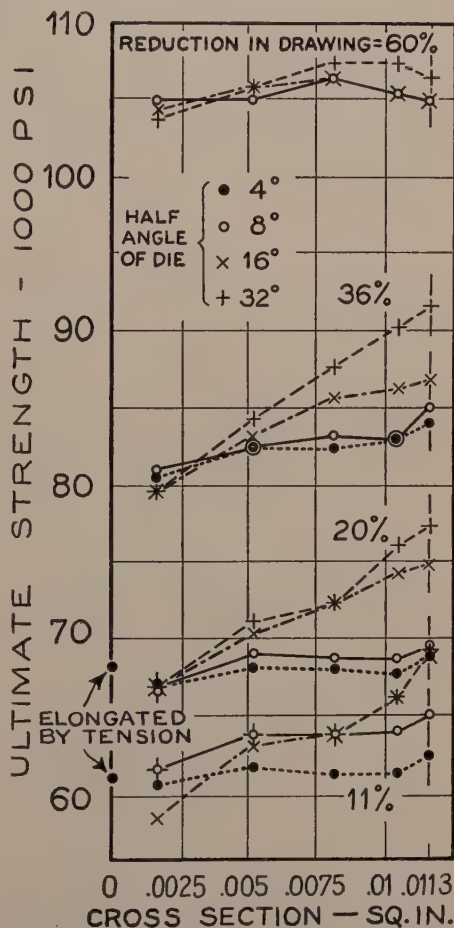


FIG. 1.—VARIATIONS IN TENSILE STRENGTH OF BRASS WIRES DRAWN THROUGH CEMENTED CARBIDE DIES, HAVING DIFFERENT ANGLES AND PICKLED TO VARIOUS CROSS SECTIONS.

63 per cent copper, 37 per cent zinc. Courtesy American Society for Metals.

Abstracted from a thesis presented to the Case School of Applied Science by G. B. Kasik in the partial fulfillment of the requirements for the B.S. degree. Manuscript received at the office of the Institute June 30, 1941. Issued as T.P. 1385 in METALS TECHNOLOGY, October 1941.

* Associate Professor, Research Assistant, and Graduate Assistant, respectively, Metallurgical Department, Case School of Applied Science, Cleveland, Ohio.

¹ References are at the end of the paper.

gliding surfaces.⁹ In drawing, such a high surface temperature would be present for only a very short time at any particular section.

No similar observations have been made, as yet, on drawn tubing. Therefore, brass tubing drawn under various conditions has been analyzed for the distribution of the strength in the cross section. These experiments constitute part of an extended research program on tubing.* It was expected that the strength distribution might also yield some indication regarding the stresses acting during drawing. The actual stress state during drawing is not known as yet; and many phenomena encountered in tubing still must be explained. This is particularly true with regard to the residual stress.¹⁰

MATERIAL AND PROCEDURE

The simplest conditions in tube drawing are encountered in sinking; i.e., drawing without an internal tool. For sinking, only the outer surface is subjected to friction; and it should be expected that the discussed irregularities are restricted to a certain depth on the outside.

Therefore several pieces of annealed cartridge-brass tubing, having varying outside diameter but a constant wall thickness of $\frac{1}{32}$ in., were sunk to an outside diameter of $\frac{1}{2}$ in., varying the type and material of the die and the reduction according to the following table:

	Steel Dies, Chromium-plated ^a			Tungsten- carbide Die ^a
Half die angle, deg.	5	$12\frac{1}{2}$	$27\frac{1}{2}$	11
Reduction in area, per cent	17	$\frac{6}{15}$ 30	16	16

^a All dies had a $\frac{1}{8}$ -in. radius connecting the working surface and the bearing.

* This program has been sponsored by the Wolverine Tube Co., Detroit, Mich. The draw bench and dies have been loaned to Case School of Applied Science by this company, which also supplied the brass and copper tubing for the investigation.

The reductions were actually measured and correspond to reductions of 6, 20 and 33 per cent of the outside diameter.

The drawing was performed on an experimental hydraulic drawing bench (Fig. 2) with a speed of 7 ft. per min. The outside of the tubing was lubricated with castor oil.

Pieces of the drawn tubing 18 in. long were cleaned with carbon tetrachloride, plugged with rubber stoppers, and pickled to a smaller outside diameter in hot dilute nitric acid. By placing the specimens on glass rods and rolling during pickling, the tube wall could be removed by various amounts uniformly within ± 0.0005 in. The specimen with the greatest amount of wall removed had a wall thickness somewhat below 50 per cent of that of the as-drawn tubing. Each piece yielded two tensile-test specimens, which were tested for ultimate strength only. The average outside diameter was measured carefully, close to ± 0.0002 in. by means of a micrometer. The testing was performed in a 10,000/60,000-lb. hydraulic Olsen testing machine.

RESULTS

The maximum load values, P , obtained in the tensile test of the various specimens are plotted in Fig. 3, versus their cross-sectional area F . The experimental points are carefully connected by a smooth trend curve, which permitted the determination of the slope or derivative $\frac{dP}{dF}$ at each particular abscissa or tubular fiber, which includes with the inside surface the area F . The ultimate strength S_T at this abscissa F is then determined by the following simple equation:

$$P = \int_{F=0}^{F=F} S_T dF$$

$$S_T = \frac{dP}{dF}$$

Such a differentiation can be performed by the elementary graphical method. How-

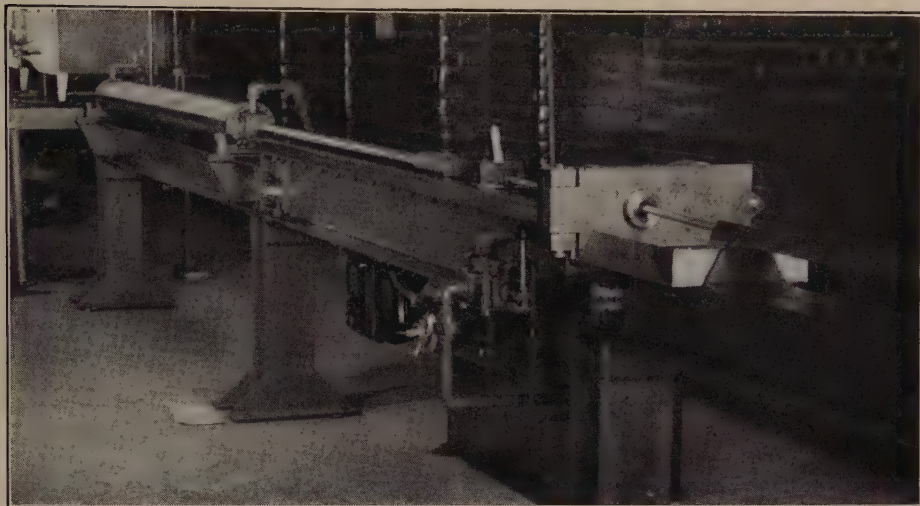


FIG. 2.—HYDRAULIC DRAW BENCH.

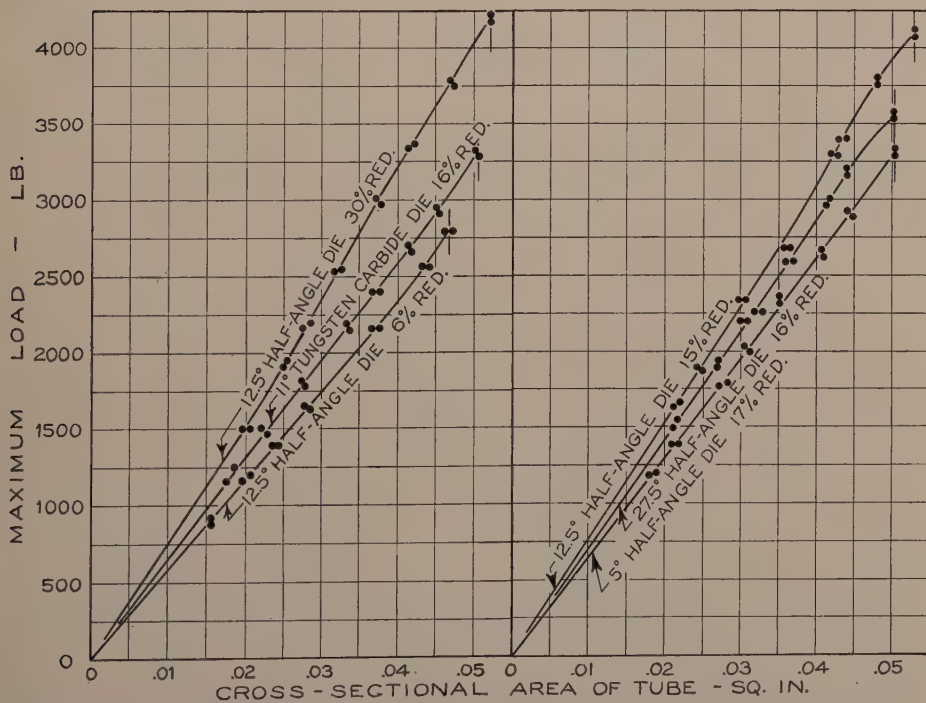


FIG. 3.—EFFECT OF REDUCTION OF SECTION BY OUTSIDE PICKLING ON MAXIMUM TENSILE LOAD OF CARTRIDGE-BRASS TUBING SUNK UNDER VARIOUS CONDITIONS.

ever, the accuracy is limited, as differentiation generally increases the errors, particularly at the ends of the curve. The results of this procedure, Fig. 4, represent-

per cent reduction with the $12\frac{1}{2}^\circ$ half-angle die, was taken from a different lot having a Rockwell F hardness of 71 and therefore being approximately 10 per cent

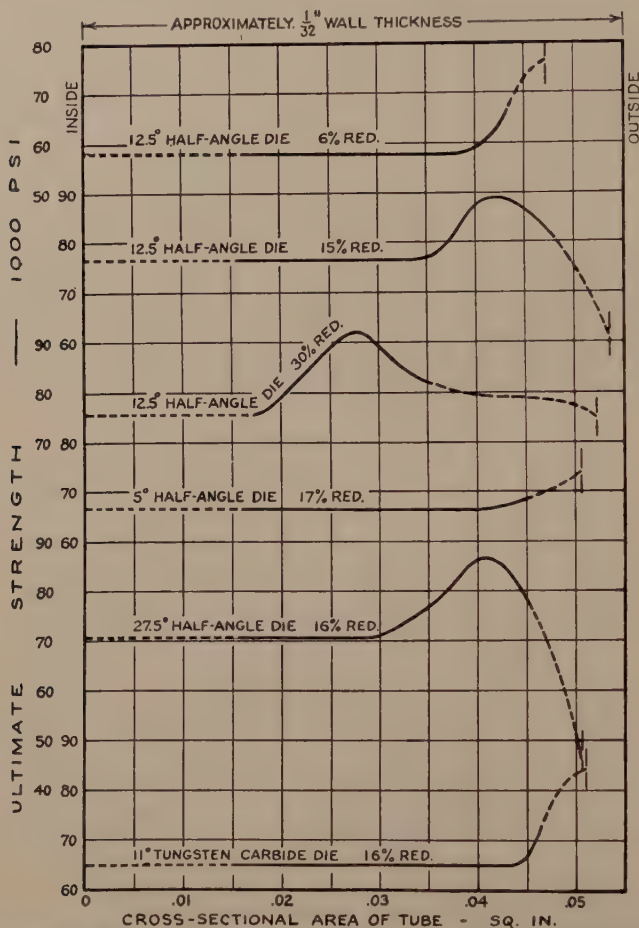


FIG. 4.—DISTRIBUTION OF TENSILE STRENGTH OVER CROSS SECTION OF VARIOUS SUNK CARTRIDGE-BRASS TUBINGS.

ing the strength distribution over the cross section of the brass tubing, drawn under various conditions are therefore somewhat subject to argument. The general trend of the curves, however, appears quite probable.

Unfortunately, only five of the six tubes investigated were drawn from the same lot of annealed tubing having a Rockwell F hardness of 60 to 65. The tubing given 15

stronger than the first lot. The strength distribution should not be materially affected by this difference; and the absolute strength values for this tubing should fit into the general pattern by uniformly reducing them by 10 per cent.

The force-area curves for the different tubes (Fig. 3) generally appear to be straight for the inner portion of the tube wall and sometimes very close to the out-

side surface. In the vicinity of the outside surface, they are usually curved concave toward the abscissas, running somewhat above the trend of the straight portion.

ing to a decreasing contact length between metal and die, affects both the average strength and the strength of the inner fiber only slightly. The differences are within

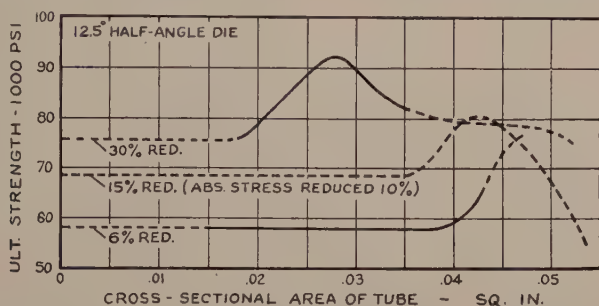


FIG. 5.—EFFECT OF REDUCTION ON STRENGTH DISTRIBUTION OF SUNK CARTRIDGE-BRASS TUBING.

The resulting strength-area curves (Fig. 4) usually show a horizontal portion on the inside and a maximum somewhere between the center fiber and the outside fiber. If this maximum is a considerable distance in from the outer surface, a low strength value is found in the outside surface fiber.

the tolerances of the measurements, 5 per cent; the strength appears to be somewhat higher if the tubing is drawn through a wide-angle die than if it is drawn through an acute die. However, the maximum is increased and shifted away from the outer surface with increasing die angle.

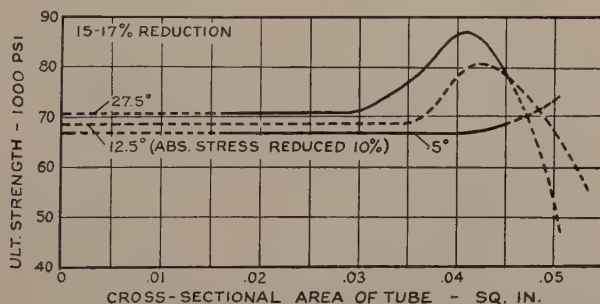


FIG. 6.—EFFECT OF DIE ANGLE ON STRENGTH DISTRIBUTION OF SUNK CARTRIDGE-BRASS TUBING.

CONCLUSIONS

Regarding the effect of the drawing conditions that have been varied in this investigation, the following conclusions can be drawn:

Increasing reductions (Fig. 5) increase the average strength. The fiber having the maximum strength may be very close to the surface with small reductions but is moved farther away from the outside surface with large reductions.

Increasing die angle (Fig. 6), correspond-

The tubing drawn with the low-friction tungsten carbide die (Fig. 4) has a strength distribution corresponding to that of tubing drawn by a smaller reduction with a chromium-plated die of approximately the same die angle.

A few additional experiments have also been made on copper tubing, given approximately 20 per cent reduction by sinking through dies having working surfaces of $1\frac{1}{8}$ and 2-in. radius.* The strength distri-

* By B. L. McMillan. The results are assembled in his B.S. thesis.

bution was found to be much the same as in the brass tubing drawn through the die having a $12\frac{1}{2}^\circ$ half-angle die. However, both the maximum and the soft skin were more pronounced in the copper tubing than in the brass tubing.

Because of the limited experimental evidence, these conclusions are somewhat open to argument, but they agree well with the previously known facts discussed in the introduction of this paper.

It thus appears that there is a tendency to create a hard skin in tube drawing, this increasing in hardness with increasing die angle and increasing in depth with increasing reduction.

The adverse tendency toward softening by annealing increases with increasing reduction and increasing die angle. This can be explained by the probable relations that while the surface heat developed increases approximately proportionally with the reduction, this surface heat is also dissipated faster as the contact area becomes larger. Also, the increase of hardness with increasing reduction and with increasing die angle will favor the softening.

The phenomena discussed in this paper have some bearing on the hardness testing of tubing. The hardness values obtained on numerous sunk tubings were found to be different for the outside and the inside, the Rockwell 15-T values being 10 to 15 units higher for the inside, the 30-T and B values being almost identical and the 45-T values being up to 25 units higher for the outside. This is readily explained by the varying strength or hardness of the different layers of a drawn brass tubing, the outside of which should appear soft if tested with a very small load, but high if tested with a load that penetrates mainly into the layer of maximum hardness. For a given reduction all the different hardness values were found to increase with increasing die angle.

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DISCUSSION

(D. K. Crampton presiding)

R. G. SPENCER,* Chicago, Ill.—I think the statement was made that iron wires, steel wires, are hard on the outside and softer on the inside. How do you measure the hardness on the outside with respect to the hardness on the inside?

G. SACHS.—I have not done any measurements on steel. As far as I remember, small indentations were made on the section of a rod.

R. G. SPENCER.—Do you draw inferences from the strength of the wire on that basis, the strength of various fibers?

G. SACHS.—Yes. I assume that the hardness is approximately proportional to the ultimate strength and yield strength of the individual fibers in the wire.

R. G. SPENCER.—The strength of various sections of a wire is a function of its fibering, too. Fibering usually is more pronounced near the middle of a wire than near its exterior.

G. SACHS.—I am not quite clear as to what you mean by fibering. Of course, in many steels segregations are present.

R. G. SPENCER.—I simply mean preferred orientation of the crystals within the wires.

G. SACHS.—Preferred orientation is more pronounced in the interior than on the exterior. The strength is higher on the outside than on the inside.

R. G. SPENCER.—After etching off the outside you measure the strength of the remaining wire?

G. SACHS.—Yes. That has been done for brass. Fig. 1 illustrates these conditions.

* Armour Research Foundation.

D. K. CRAMPTON,* Waterbury, Conn.—With small-diameter wire, it would seem to me, it would be most difficult to pick up the presence of a thin surface layer by the procedure you describe of making hardness tests on a cross section.

G. SACHS.—It would be extremely difficult to show the presence of a soft layer on heavy stock; however, in our experiments the thin, soft surface layer apparently is a substantial portion of the whole tube section.

C. S. SMITH,† Waterbury, Conn.—Have the authors made any attempt to measure the distribution of yield strength across the tube sections?

G. SACHS.—We did, and obtained approximately the same results. But the values were not accurate enough to enable an accurate determination of the slope.

S. TOUR,‡ New York, N. Y.—I would not disagree on the soft layer on the surface, but I would like to inquire with regard to the explanation that the soft surface is due to annealing by the surface heat generated by friction during drawing. If this is true, the depth of the soft layer should be controlled by the speed of drawing. The faster the draw, the thinner should be the soft layer, especially if the draw is through a fairly cool die. Has any such effect been found?

G. SACHS.—I have been thinking about this problem. My reasoning so far is that if metal is drawn reasonably fast, all the heat is stored for a very short time in the metal. There is probably little dissipation of heat during the actual flow. The dissipation starts when the metal leaves the die.

D. K. CRAMPTON.—With regard to a thin softened surface layer, could this be overcome by extremely slow drawing together with very efficient cooling?

G. SACHS.—I believe it should be possible to eliminate a soft layer on the surface by very slow drawing.

D. K. CRAMPTON.—Were these tubes straightened in any manner after they were sunk, or were they tested first as taken from the drawbench?

G. SACHS.—They were tested as drawn.

D. K. CRAMPTON.—This paper and the one you presented yesterday (p. 348) speak of thin-walled tubes. Is there any reason why the general procedure described should not be applicable to heavy-walled tubes?

G. SACHS.—The method of stress measurements used applies only to thin-walled tubing. The accurate stress distribution in heavy-walled tubing must be determined by a different method, which I developed in 1927 and which has been used for this purpose to a considerable extent.

D. K. CRAMPTON.—What I had in mind was the change in wall thickness of a tube due to sinking. This depends on the initial ratio of wall thickness to diameter. With a thin-walled tube—one having a small ratio of wall thickness to diameter—the thickness invariably increases on sinking. With heavy-walled tubes having a large ratio of wall thickness to diameter, the wall thickness decreases on sinking. This differing behavior depending on initial ratio of wall thickness to diameter might make a considerable difference with the stress distribution found when investigating different tubes by your procedure.

G. SACHS.—So far, our work concerns thin-walled tubing. It is dangerous to extrapolate.

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†Research Laboratory, American Brass Co.

‡Lucius Pitkin, Inc.

Residual Stress in Sunk Cartridge-brass Tubing

BY G. SACHS,* MEMBER, AND G. ESPEY,† STUDENT ASSOCIATE A.I.M.E.

(Philadelphia Meeting, October 1941)

It is well known that high residual stresses are created in tubing by the sinking process, in which no internal tool or mandrel is used.¹⁻⁴ In this process, the wall thickness is usually slightly increased.^{4,5} In tube drawing with a plug, the residual stresses are gradually reduced with increasing reduction of wall, and, by the conventional approximation methods of stress measurement, no stress is detected in tubing in which the wall reduction is over 50 per cent of the total reduction in cross-sectional area.^{1,6} It has also been observed that higher stresses are set up by the use of wide-angle dies than by acute dies.²

The actual stress distribution in drawn tubing has been investigated by a few workers,⁷⁻⁹ but has not been related to the conditions of the drawing process.

Some attempts have been made to correlate accelerated cracking tests for stresses in brass products with the magnitude of the circumferential stresses and the condition of the metal.¹⁻¹⁰

MATERIALS AND PREPARATION

The material used in this experiment was commercial cartridge-brass (70 per cent Cu, 30 per cent Zn) tubing in the straightened and annealed condition.‡ This tubing was of various outside diameters and had a wall thickness of 0.032 in. It was sunk to ½-in. outside diameter by means of an

experimental 10,000-lb. hydraulic drawbench, with a maximum drawing speed of 8 ft. per minute.

All dies were of ½-in. diameter. Various die materials and contours were used in order to study the effect of die design on residual stresses in the tubing; the specifications for the dies are given in Fig. 1. Castor oil was used throughout as lubricant.

Chattering occurred in sinking some of the tubing, particularly when dies having the more acute angles were used, but the tubes showing chatter marks did not differ markedly from those with a smooth surface regarding the magnitude of residual stress. The source of the chattering has not yet been revealed.

The wall of the tubing becomes thicker during sinking, as previously observed.^{4,5} The increases in wall thickness were 3, 7 and 9.5 per cent on the average for 6, 20 and 33 per cent reductions in diameter, no effect of the contour being noticeable. The reductions mentioned throughout this investigation do not consider this fact, but are reductions of the outside diameter.

For the evaluation of the residual stress two fundamentally different methods were used. The approximation method^{1,11} of splitting a certain length of tubing was employed to obtain a bird's-eye view of the effect of various drawing conditions on the circumferential stress measured by the diameter change occurring on splitting. For

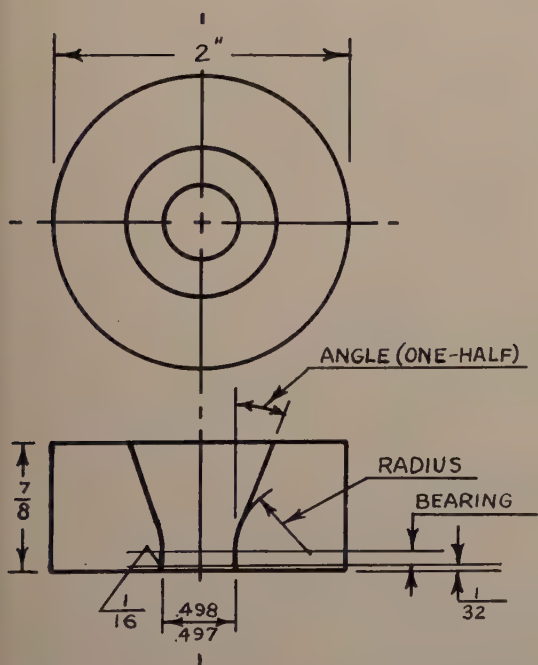
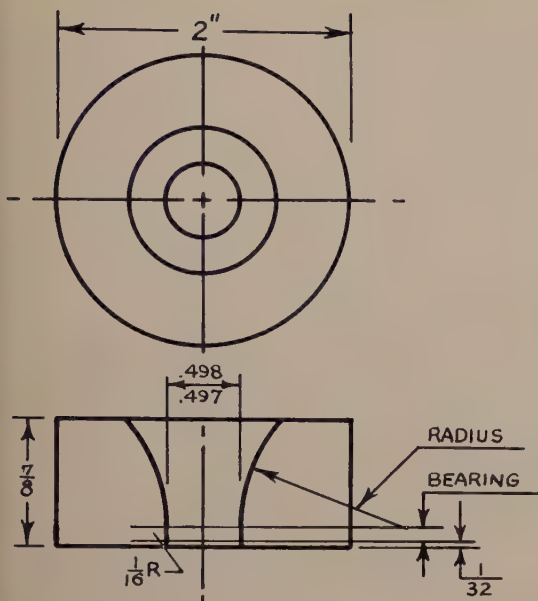
Abstracted from a thesis presented to the Case School of Applied Science by G. Espey in partial fulfillment of the requirements for the M.S. degree. Manuscript received at the office of the Institute July 7, 1941. Issued as T.P. 1386 in METALS TECHNOLOGY, October 1941.

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† Research Assistant, Case School of Applied Science.

¹ References are at the end of the paper.

‡ The present paper constitutes part of an extended investigation on tube drawing, sponsored by the Wolverine Tube Co., Detroit, Mich. We are indebted to this company for the loan of the experimental drawbench and auxiliary equipment, and for the preparation of the metal.



DIE NO	RADIUS INCHES	BEARING INCHES	PLATING
0	$\frac{1}{8}$	$\frac{1}{16}$	CHROMIUM
1	$\frac{1}{8}$	$\frac{1}{64}$	"
2	$\frac{1}{8}$	$\frac{1}{32}$	"
3	$\frac{1}{8}$	$\frac{1}{8}$	"
4	$\frac{1}{4}$	$\frac{1}{4}$	"
5	2	$\frac{1}{16}$	"
6	$\frac{1}{8}$	$\frac{1}{16}$	NO PLATE
25	$\frac{7}{32}$	$\frac{1}{16}$	CHROMIUM
26	$\frac{7}{16}$	$\frac{1}{16}$	"

MATERIAL:

BETHLEHEM "XX" STEEL
HARDEN — ROCK "C" 60-65
GRIND AND POLISH HOLE
CHROME PLATE
FINISH POLISH

	ONE-HALF ANGLE	BEARING INCHES	RADIUS INCHES
11	2.5	$\frac{1}{16}$	$\frac{1}{2}$
12	5.0	$\frac{1}{16}$	"
13	7.5	$\frac{1}{16}$	"
14	10.0	$\frac{1}{16}$	"
15	12.5	$\frac{1}{16}$	"
16	7.5	$\frac{1}{64}$	"
17	7.5	$\frac{1}{32}$	"
18	7.5	$\frac{1}{8}$	"
19	7.5	$\frac{1}{4}$	"
20	27.5	$\frac{1}{16}$	"
W.C.	(TUNGSTEN CARBIDE)		
	11	$\frac{1}{8}$	$\frac{1}{2}$

FIG. 1.—CONTOURS OF DIES.

the determination of the complete stress distribution, a modification of Dawidenkow's⁷ method was developed, consisting of pickling, splitting and slitting a number of specimens. This method, and the factors

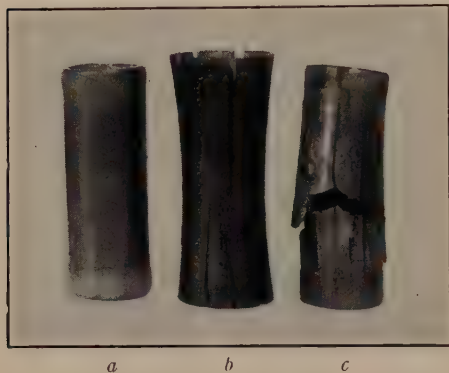


FIG. 2.—SPECIMENS FOR CORROSION CRACKING.
a. Specimen with paraffined ends.
b. Cracked specimen with unprotected ends.
c. Cracked specimen with paraffined ends.

influencing the accuracy of such stress measurements, have been described.¹²

For the accelerated cracking tests, a 1 per cent mercurous nitrate solution (990

factor $\frac{1000}{t}$ is referred to in this investigation as cracking tendency.

In order to obtain a simple picture of the surface stresses present, rather than the average end distribution, of both circumferential and longitudinal stresses, the ends of the specimens were dipped in paraffin (Fig. 2a) to protect them from the mercurous nitrate solution. The specimens used were $1\frac{1}{4}$ to $1\frac{1}{2}$ in. long and the paraffin tips were approximately $\frac{3}{16}$ in. long, thus leaving an exposed tubing surface approximately 1 in. long. These tips permitted no end attack and prevented the specimen from fraying at the ends (Fig. 2b), thereby forcing the longitudinal stresses to be relieved through the formation of circumferential cracks (Fig. 2c), and avoided a premature cracking caused by the maximum stress on the surface of the cut. The surface of the specimens used in the cracking test was cleaned, before the ends were dipped in paraffin, by first wiping the surface with a cloth saturated with carbon tetrachloride and then washing the specimens in a series of three baths of isopropyl

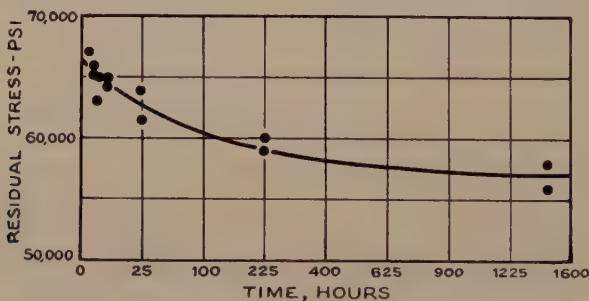


FIG. 3.—EFFECT OF TIME (AT ROOM TEMPERATURE) AFTER SINKING ON RESIDUAL STRESS.

c.c. H_2O , 10 grams HgNO_3 , 10 c.c. conc. HNO_3) was selected. With a 10 per cent solution, as frequently used, the fine cracks developed in many specimens were covered with mercury and could not be detected. The temperature of the solution was $80^\circ \pm 5^\circ\text{F}$. ($26^\circ \pm 3^\circ\text{C}$.).

The cracking time t was determined with a stopwatch, probably within 3 sec. The

ether, leaving them in each wash for approximately 20 seconds.

STABILIZATION OF RESIDUAL STRESSES

To determine the amount of stress relief occurring in drawn tubing at room temperature, specimens were cut from one tube and stored at room temperature for various lengths of time. The results (Fig. 3) show

that the magnitude of the stress relief in the as-drawn tubing was approximately 10 per cent between 10 hr. and 90 days.

In the light of the results, it was assumed that during the pickling of different specimens of tubing for various lengths of time (up to 15 min. maximum) at the relatively high temperature of 160° to 180°F. (70° to

EFFECT OF DRAWING CONDITIONS ON MAGNITUDE OF RESIDUAL STRESS AS REVEALED BY SPLITTING METHOD

The results of the tests show that the residual stress in drawn tubing depends primarily upon two factors (Figs. 5 and 6).

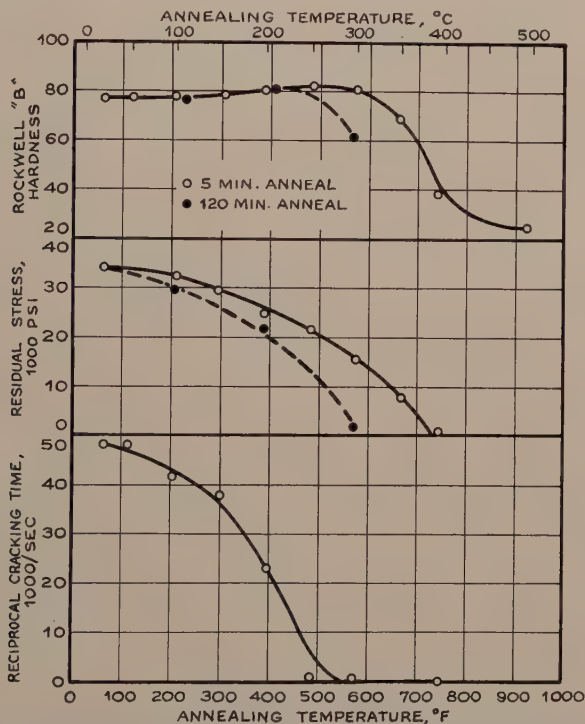


FIG. 4.—EFFECT OF TEMPERATURE AND TIME OF ANNEAL ON HARDNESS, RESIDUAL STRESS AND CRACKING TENDENCY OF COMMERCIAL HARD CARTRIDGE-BRASS TUBING (CLARK AND HIPPLER).

80°C.) a small fraction of the stresses in the various specimens would be relieved. Therefore, in order to minimize the errors involved by storing at room temperature and by pickling for various times, the practice of annealing all tubing 15 min. at 212°F. (100°C.) was adopted. It was found that the residual stress of tubing stored one week at room temperature after sinking was lowered 8 per cent by this anneal. This agrees with previous results^{13,14} (Fig. 4).

It increases with both, increasing reductions and decreasing contact length between die metal or increasing "die angle."⁴ Bell-shaped dies produce residual stress of approximately the same or a slightly lower magnitude than conical dies having a taper or "effective die angle" corresponding to the chord of the contact length of the bell-shaped die.

The effects of die contour and reduction on the residual stress appear to be fundamentally the same for sunk brass tubing

and for drawn wire.⁵ The extensive investigation of wire has shown that the magnitude of the residual stress corresponds to the magnitude of nonuniform flow or shear in the surface fibers of the wire. This also

EFFECT OF DRAWING CONDITIONS ON CRACKING TENDENCY

The cracking tendency of the drawn tubing also increases with both the die angle



FIG. 5.—EFFECT OF DIE ANGLE AND REDUCTION ON RESIDUAL CIRCUMFERENTIAL STRESS IN CARTRIDGE-BRASS TUBING, SUNK WITH TAPERED CHROMIUM-PLATED DIES.

results in an increased strength of the surface metal. A similar effect has been observed in the sunk tubing.⁶

With increasing length of "bearing" or "land" (Fig. 1), the residual stress decreases (Figs. 7 and 8). This reduction is considerably larger with a bell-shaped die than with a conical die. Dies of different materials, such as steel and cemented carbide (compare Fig. 17 with Fig. 21), or having a different surface, such as steel or chromium (Fig. 9), other conditions being equal, produce almost the same magnitude of residual stress. It appears that the stresses are slightly higher after drawing with a chromium-plated die than with an unplated steel die.

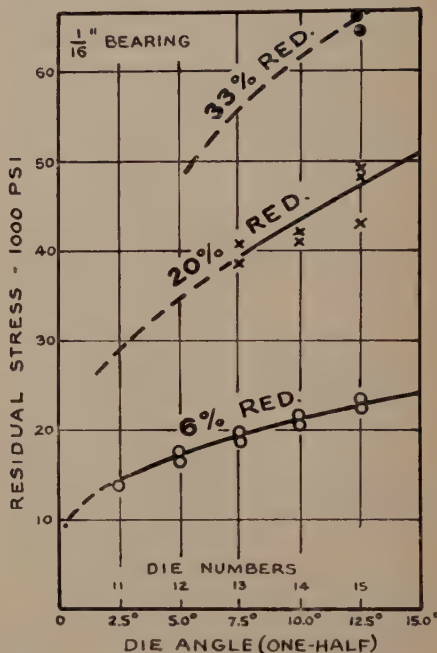


FIG. 6.—EFFECT OF DIE RADIUS AND REDUCTION ON RESIDUAL CIRCUMFERENTIAL STRESS IN CARTRIDGE-BRASS TUBING, SUNK WITH RADIUSED CHROMIUM-PLATED DIES.

(Fig. 10) and the reduction (Fig. 11). However, with the smallest reduction, 6 per cent, performed with the investigated $12\frac{1}{2}^\circ$ half-angle die, the cracking tendency is almost zero. This corresponds to previous observations^{1,10,14} that no cracking occurs in drawn tubing if the residual stress as determined by the splitting method is below 12,000 to 15,000 lb. per sq. inch.

The first cracks to appear in these tests generally have been found to be longitudinal in nature; i.e., caused by circumferential stress. However, after extended exposure to the mercurous nitrate solution circumferential cracks also usually become visible (Fig. 2c). These circumferential cracks, caused by the longitudinal stress

not relieved by the first longitudinal cracks, therefore measures a secondary circumferential cracking tendency (Figs. 22 and 23). It appears that this secondary crack-

DISTRIBUTION OF RESIDUAL STRESS

Because of the tedious procedure, the effect of only a few selected drawing condi-

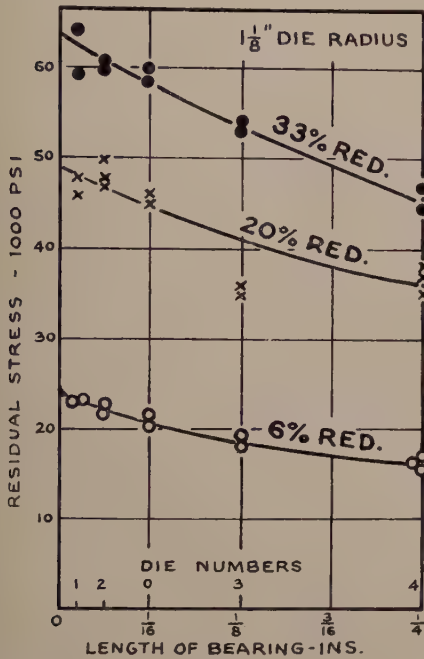


FIG. 7.

FIGS. 7 and 8.—Effect of bearing length on residual stress in sunk, commercial cartridge-brass tubing.

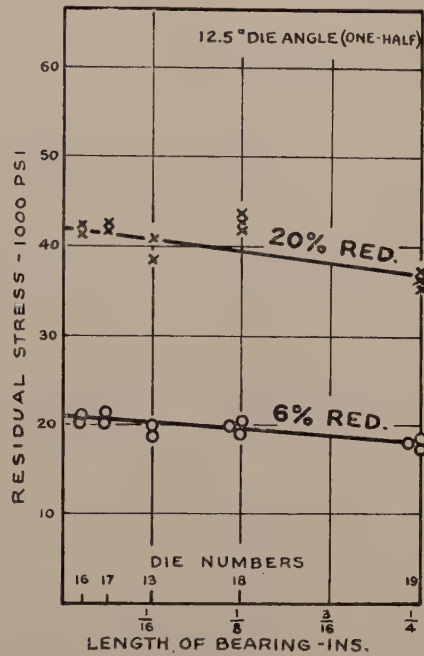


FIG. 8.

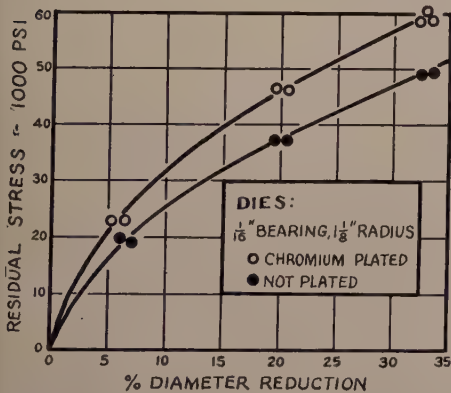


FIG. 9.—Effect of die surface on residual stress in sunk cartridge-brass tubing.

tions on the distribution of the residual stress could be investigated. A number of

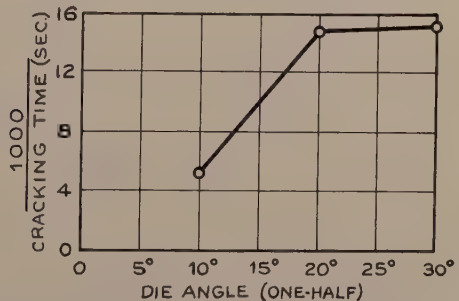


FIG. 10.—Effect of die radius on cracking tendency of cartridge-brass tubing, sunk with tapered chromium-plated dies.

ing tendency also increases with increasing die angle, but reaches a maximum with medium reductions.

specimens in each condition were subjected to outside and inside pickling, removing various amounts of the wall thickness;

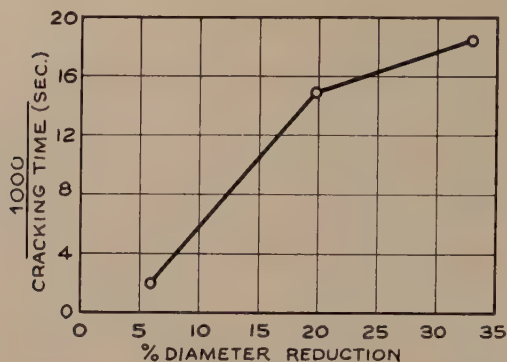


FIG. 11.—EFFECT OF REDUCTION ON CRACKING TENDENCY OF CARTRIDGE-BRASS TUBING, SUNK WITH A $12\frac{1}{2}^\circ$ HALF-ANGLE DIE.

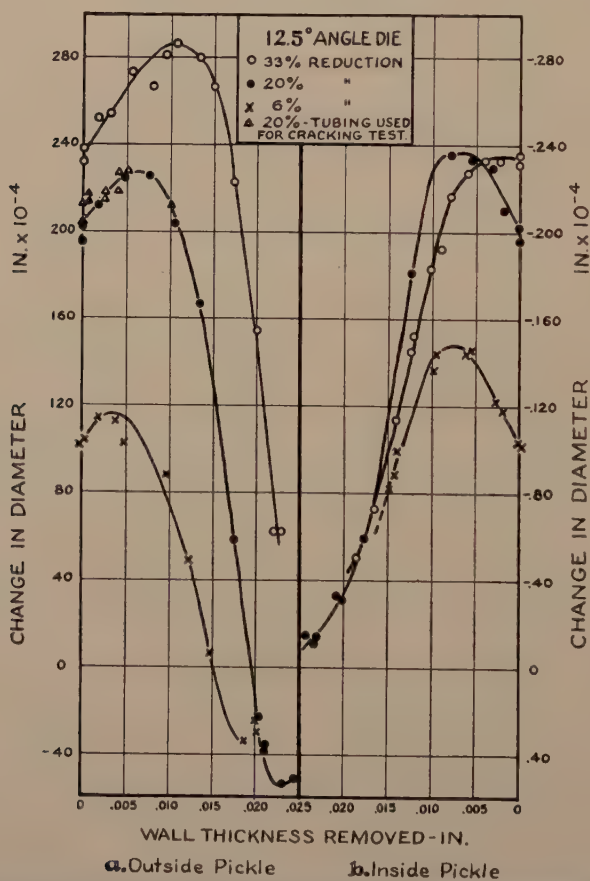


FIG. 12.—DIAMETER CHANGES OBSERVED ON SPLITTING SUNK CARTRIDGE-BRASS TUBING SPECIMENS PICKLED BY VARIOUS AMOUNTS FROM THE OUTSIDE AND INSIDE.

then they were split, the diameter change was determined, a tongue was slit and its deflection measured. The diameter changes (Figs. 12 and 13) and deflections of the tongue (Figs. 14 and 15) are plotted, and the respective distributions of the circumferential and longitudinal stress calculated

A probable explanation for the observed stress distribution will be discussed later.

CRACKING TESTS ON PICKLED SPECIMENS

In order to correlate stress distribution and cracking tendency, outside pickled

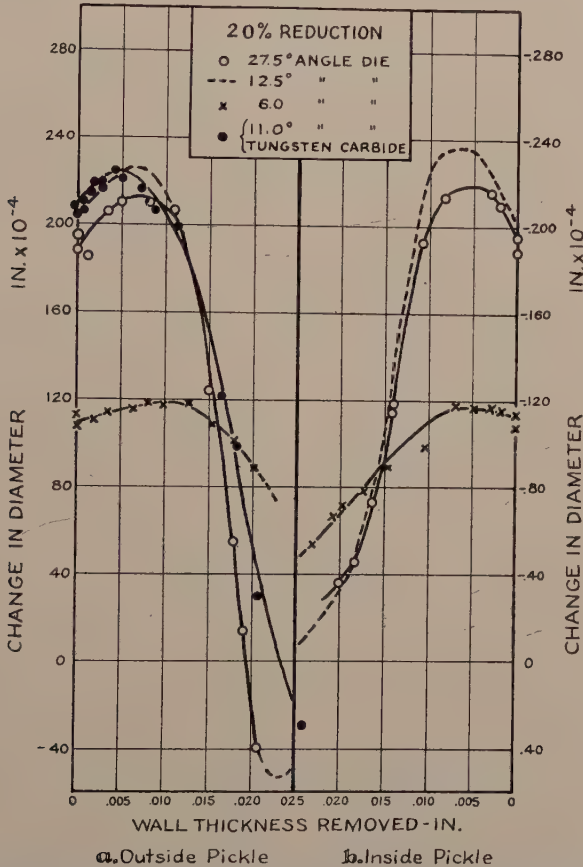


FIG. 13.—DIAMETER CHANGES OBSERVED ON SPLITTING SUNK CARTRIDGE-BRASS TUBING SPECIMENS, PICKLED BY VARIOUS AMOUNTS FROM THE OUTSIDE AND INSIDE.

(Figs. 16 to 21). The procedure is described in detail in the previous paper.¹²

The resulting stress distributions are rather complex, particularly of the longitudinal stress, which is sometimes very low at the surface or has a minimum close to the outer surface and very high in a layer some distance apart from the outer surface.

specimens cut from several pieces of tubing were also subjected to cracking tests. The results (Figs. 22 and 23) show that the cracking tendency of tubing may vary considerably with the pickling treatment, and that either circumferential or longitudinal cracks are formed first, depending upon the amount of metal removed on

pickling. This may explain some controversial observations on cracking and the frequently reported sensitivity of the mercury test regarding slight changes of testing conditions.

the surface, caused by an increase of the residual stress with increasing distance from the surface. When such a hump was detected, this time was considered as the cracking time.

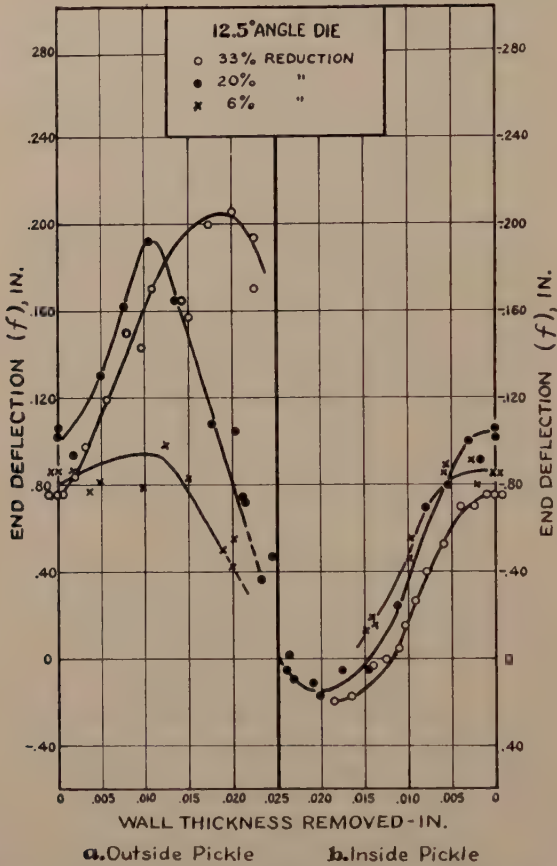


FIG. 14.—DEFLECTIONS OF TONGUE SLIT FROM CARTRIDGE-BRASS TUBING SPECIMENS, PICKLED BY VARIOUS AMOUNTS FROM THE OUTSIDE AND INSIDE.

In these tests, the first appearance of both longitudinal and circumferential cracks was determined. While circumferential cracks could be detected readily after longitudinal cracks had formed, the reverse was difficult to observe.

In a number of specimens, humps were observed before cracks formed at the surface in the center of the humps. This is attributed to initial cracking underneath

CORRELATION OF STRESS DISTRIBUTION AND CRACKING TENDENCY

It will be expected that the cracking tendency is primarily determined by the residual stresses present in the extreme surface layer. This stress for a pickled specimen is not the same as that shown in the stress-distribution curves (Figs. 17 and 21) at the considered point before pickling;

but it is changed a certain amount by the pickling process. This amount is the negative value of the force removed on pickling and distributed over the remaining wall

stresses being equal. This can be explained by the fact that the cohesive strength of the metal across the fiber is usually somewhat lower than with the fiber. It also ap-

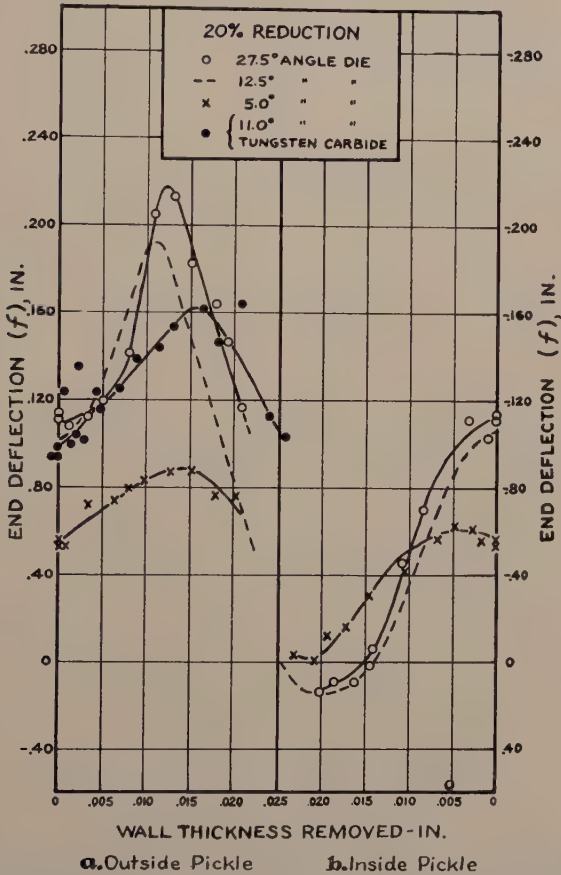


FIG. 15.—DEFLECTIONS OF TONGUE SLIT FROM CARTRIDGE-BRASS TUBING SPECIMENS, PICKLED BY VARIOUS AMOUNTS FROM THE OUTSIDE AND INSIDE.

section. This calculation can be readily carried out, resulting in the surface-stress curves shown in Figs. 24 and 25.

The comparison with the curves for cracking tendency (Figs. 22 and 23) reveals a close relation between surface stresses and cracking tendency. The trend of both types of curves is very similar.

Minor deviations indicate that the circumferential cracking tendency is somewhat lower than the longitudinal, the

pears that the cracking tendency is higher for a given surface stress if it is backed up by an increasing stress than when it is backed up by a decreasing stress.

Again, the cracking tendency becomes zero if the surface stress is lower than a certain amount, somewhere between 10,000 and 20,000 lb. per sq. inch.¹

DISCUSSION OF RESULTS

The distributions of longitudinal and circumferential stresses are quite different,

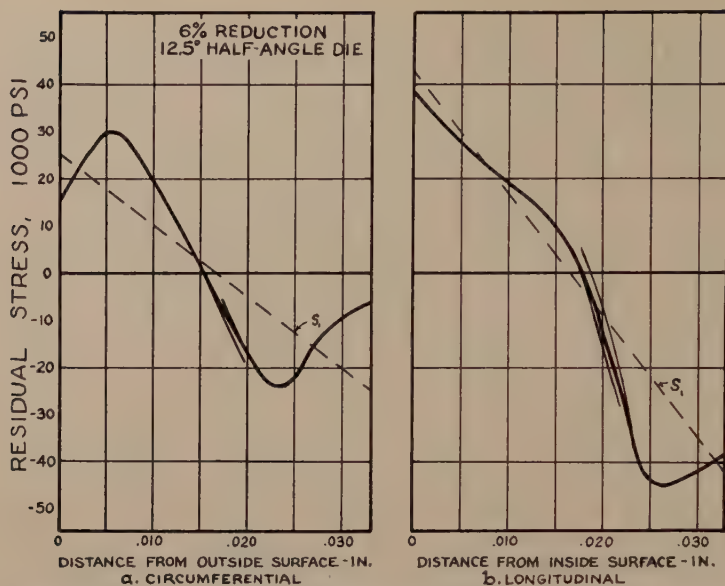


FIG. 16.—DISTRIBUTION OF CIRCUMFERENTIAL AND LONGITUDINAL STRESS IN CARTRIDGE-BRASS TUBING.

Dotted line indicates stress s_1 derived from approximation method.

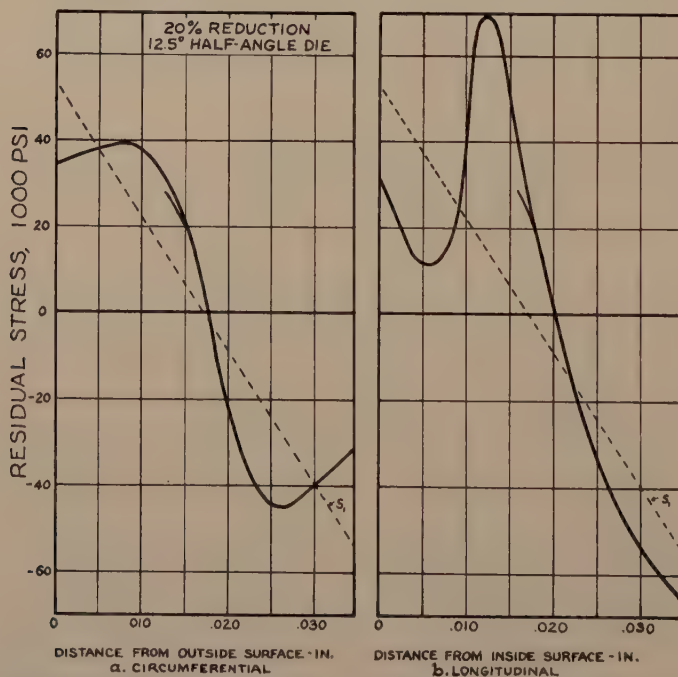


FIG. 17.—DISTRIBUTION OF CIRCUMFERENTIAL AND LONGITUDINAL STRESS IN CARTRIDGE-BRASS TUBING.

Dotted line indicates stress s_1 derived from approximation method.

both varying in a complex manner with the various factors involved in drawing.

The distribution curve for longitudinal stress usually exhibits a high tension maxi-

um and the larger-angled dies, a minimum may occur close to the outer surface with a definitely higher stress at the surface.

The distribution curves for circumferen-

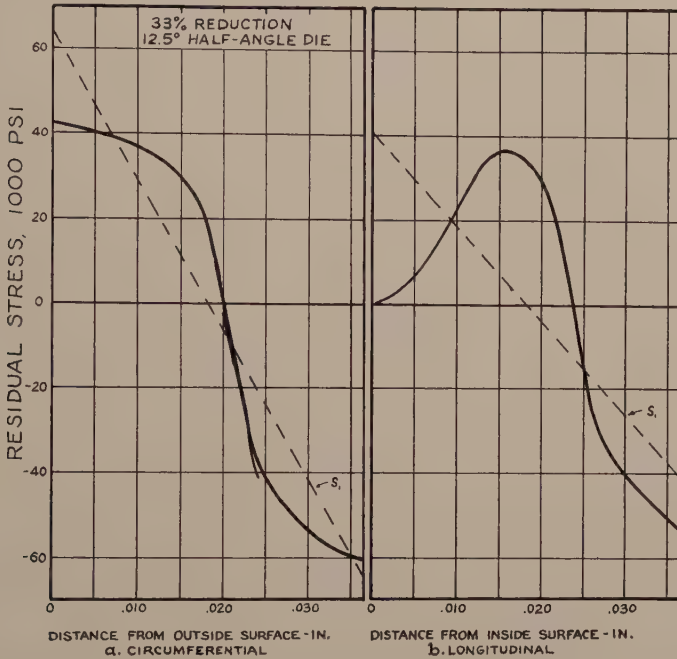


FIG. 18.—DISTRIBUTION OF CIRCUMFERENTIAL AND LONGITUDINAL STRESS IN CARTRIDGE-BRASS TUBING.

Dotted line indicates stress s_1 derived from approximation method.

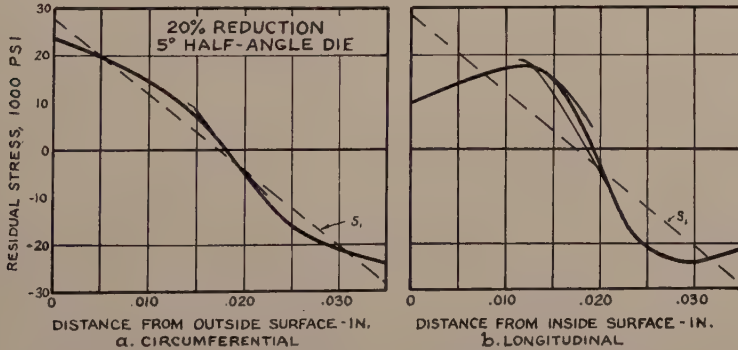


FIG. 19.—DISTRIBUTION OF CIRCUMFERENTIAL AND LONGITUDINAL STRESS IN CARTRIDGE-BRASS TUBING.

Dotted line indicates stress s_1 derived from approximation method.

um some distance in from the outside surface of the tube wall, while the compression maximum is usually very close to or at the inner surface. With medium reductions

tial stress do not deviate as much from a straight line as do the longitudinal curves; however, they often show maxima some distances from the outer and inner wall

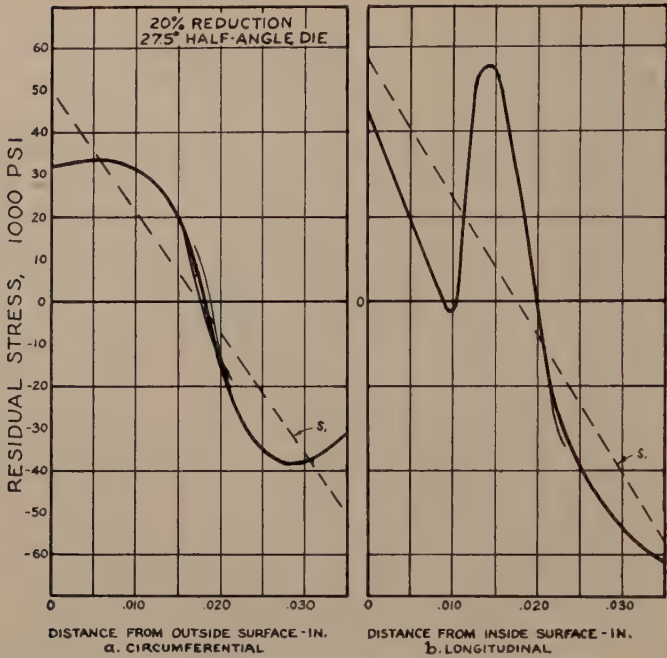


FIG. 20.—DISTRIBUTION OF CIRCUMFERENTIAL AND LONGITUDINAL STRESS IN CARTRIDGE-BRASS TUBING.

Dotted line indicates stress s_1 derived from approximation method.

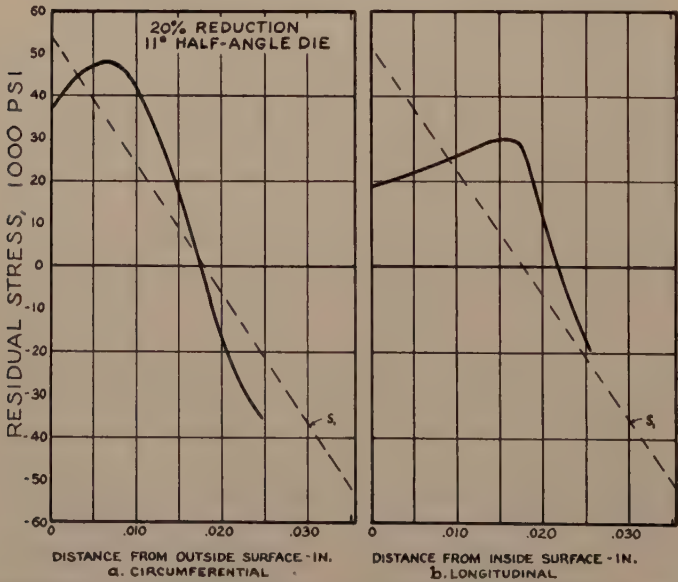


FIG. 21.—DISTRIBUTION OF CIRCUMFERENTIAL AND LONGITUDINAL STRESS IN CARTRIDGE-BRASS TUBING SUNK WITH A CEMENTED CARBIDE DIE.

Dotted line indicates stress s_1 derived from approximation method.

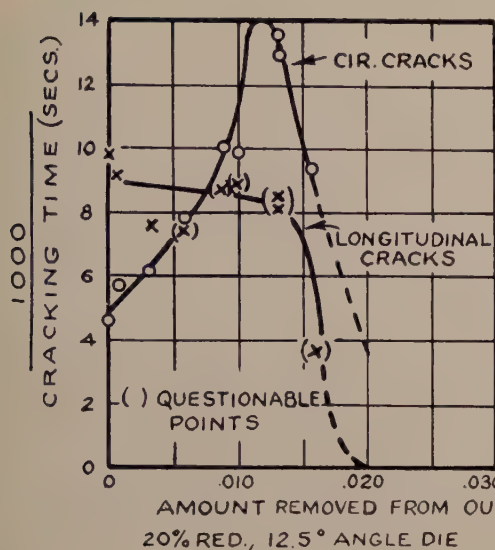


FIG. 22.

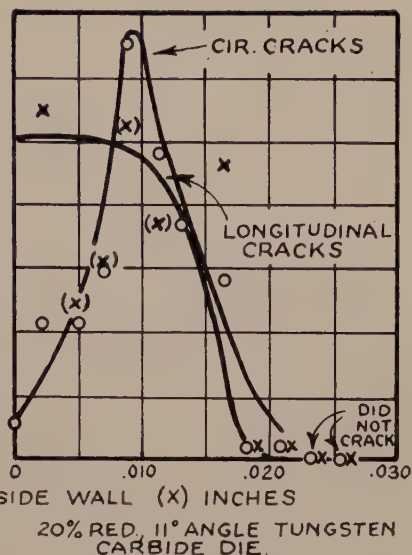


FIG. 23.

FIGS. 22 AND 23.—CRACKING TENDENCY OF SUNK CARTRIDGE-BRASS TUBING, SPECIMENS PICKLED BY VARIOUS AMOUNTS FROM THE OUTSIDE.

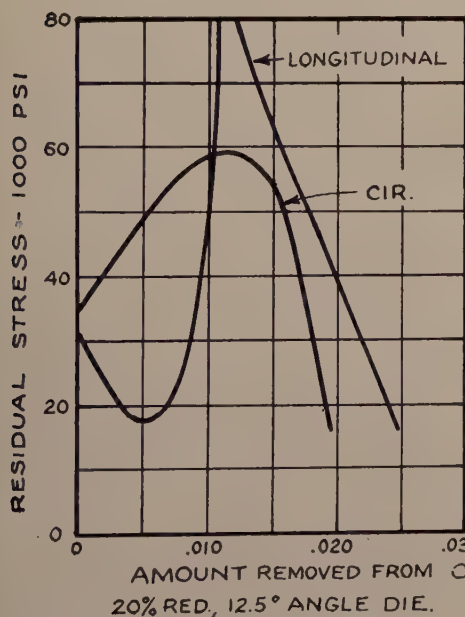


FIG. 24.

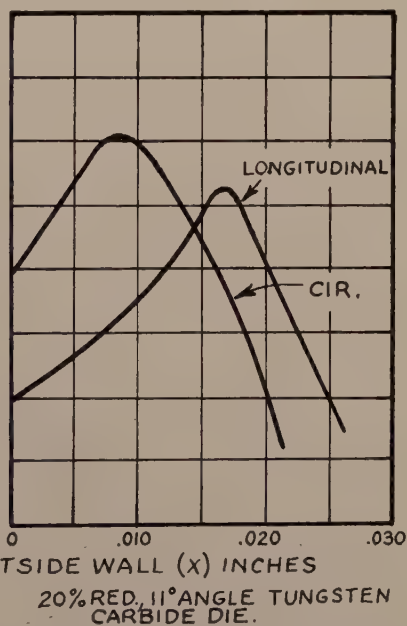


FIG. 25.

FIGS. 24 AND 25.—MAGNITUDE OF SURFACE STRESSES IN SUNK AND PICKLED CARTRIDGE-BRASS TUBING.

surfaces. The deviation becomes greater with decreasing reduction and increasing die angle (i.e., decreasing contact length).

Attempts have been made to explain the deviation of residual stresses throughout a wire or tube wall from a linear distribution by a relieving effect, taking place during drawing because of heat of friction at the surface in addition to the heat developed in the working of the metal.^{17,18} This accounts for the low stresses on the outside surface shown by some of the curves and also explains why the maxima are farther from the surface in the tubes having higher reductions. Some experiments also show a drop in strength at the surface of brass and copper tubing.¹⁶

In Figs. 17*b* and 20*b* the increase in longitudinal stresses at the surface may be due to a cooling effect resulting from less severe working in the radius section (where the "effective" angles are small) and in the bearing section.

The tension at the outer surface, which is the principal factor in determining the cracking tendency, may be larger either in the circumferential or the longitudinal direction, depending upon the drawing conditions. This explains the fact that cracking may be either in the longitudinal or circumferential direction, depending upon the relative magnitudes of circumferential and longitudinal stresses.

In most of the tubing investigated, the circumferential outside surface stresses were higher than the corresponding longitudinal stresses. However, upon sinking with a small-angle die the longitudinal stresses at the surface are larger than the circumferential stresses, Figs. 16*b* and 16*a*, respectively.

Previous investigations on the distribution of residual stress in tubing⁷⁻⁹ have been performed on tubing with a much heavier wall than that investigated here. This may explain why no irregularities in the stress distribution, particularly close to the surfaces, have been previously

observed. From the laws of thermal conductivity it is expected that only a very thin layer can be heated in cold-working to a temperature high enough to induce softening. Stress measurements on heavily-walled tubing, however, reveal only the average stress in comparatively thick surface layers and not the variations within these layers.

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DISCUSSION

(L. S. Fletcher presiding)

S. TOUR,* New York, N. Y.—I would like to try to tie together the skin described in Dr. Sachs' previous paper and the skin in this paper. It is difficult to get down to the last fraction of a thousandth of an inch of the skin and determine its state of stress. The curves in this second paper would indicate that the skin has less tension stress in it than does the metal underneath.

It might be that the skin on the surface was in compression. It would seem that it should be in compression if the theory of the softening due to skin annealing is true.

During drawing the brass is in a state of tension. If the skin is annealed during drawing, it no longer carries any tension. After drawing

* Lucius Pitkin, Inc.

the tension force is removed and the metal recovers. This recovery will put the skin in a state of compression.

The compression layer may be a fraction of a thousandth of an inch thick and therefore difficult to measure. Beyond that fraction of a thousandth there may be a tension area. The stress-distribution curve would be radically different from that shown in the paper if it were true that the skin were under compression. That it is under compression is indicated by the radical changes in mercury cracking resulting from a pre-pickle. If mercury cracks occur only in material under tension, tending to tear the grains apart, a pre-pickle in nitric acid to remove a skin under compression would make a radical change in resistance to mercury cracking. This has been observed and reported in a paper presented last winter.

The curves presented in the second paper, in so far as they concern this outer skin, indicate that the outer skin is still in tension. This has not been proved. There is a decided possibility that the skins are in compression.

G. SACHS.—When we started these experiments we were hoping to obtain some conclusive results, but, so far, the curves appear to be so complex that we do not know how to evaluate them.

No cracking would occur if the surface stress were below, say, 15,000 lb. per sq. in.; whether it is compression, or tension (below that value) would not make much difference.

We could not make the curves look much simpler than they now look and we are at a loss to explain the irregularities that obviously occur at the surface.

Of course, there is always the possibility that the experimental technique is faulty in some respects, but so far we cannot do anything but report the results and wait for someone else to point out modifications or wrong assumptions.

A. KATZ,* Detroit, Mich.—In examining the angles and bearing lengths of these dies, I notice that some of them would cause the

tubes to "suck" (tube after drawing is smaller than the die). Did your tubes come out smaller than the die? Did that make any difference?

G. SACHS.—As far as I can remember, we had some effect like that, a thousandth or two undersize in diameter when using large die angles.

A. KATZ.—The use of short bearings ($\frac{1}{8}$ in.) and large angles (45° included) in the sinking of soft steel tubing would result in the tubes being five or ten thousandths of an inch smaller than the die. The surface of the tube would also appear different.

D. K. CRAMPTON,* Waterbury, Conn.—I was interested in the "humps" you refer to, where there was a fracture beneath the surface. If these cracks or fissures were in a plane parallel to the surface, might they not indicate the presence of high radial stresses in addition to stresses in the two directions measured?

G. SACHS.—Circumferential and radial stresses in a tubing or rod are not independent but correlated. The radial stress is generally lower than the circumferential. Thus, it is difficult, if not impossible, to differentiate between circumferential and radial stress.

D. K. CRAMPTON.—I was referring to failures in a plane parallel to the surface, which is what would be visualized when you speak of humps. In other words, are these humps not evidence of a cleavage on a plane parallel to the curved tube surface?

G. SACHS.—I did not get your question at first. We did not notice any laminating of the metal. I would assume that, in a thin-walled tubing, the radial stresses are small.

D. K. CRAMPTON.—Even in thin-walled tubing it would appear there should be no fundamental reason why there could not be radial stresses, and this would certainly be true as the tube wall increases.

*Bundy Tubing Co.

* Director of Research, Chase Brass & Copper Co.

Effect of Cold-work and Annealing upon Internal Friction of Alpha Brass

BY CLARENCE ZENER,* JUNIOR MEMBER, HOWARD CLARKE,* AND CYRIL STANLEY SMITH,†
MEMBER A.I.M.E.

(Philadelphia Meeting, October 1941)

THE importance of cold-working in the fabrication of metals is in marked contrast with our ignorance as to the nature of the accompanying internal changes. The failure of the usual methods of testing to provide a consistent picture of these internal changes has given the incentive for the present program of investigating the effect of cold-working upon the internal friction of metals measured at small strain amplitudes.

It has previously been shown^{1,2,3}, that the internal friction introduced by cold-work is removed by annealing at comparatively low temperatures. In the present paper the following additional factors are investigated: (1) frequency of measurement, (2) amount of cold-work, (3) temperature of measurement. Special care was taken to minimize the internal friction due to causes other than cold-work.

The present paper is purely experimental, the authors believing that any conclusions drawn from this work as to the nature of the internal changes accompanying cold-work would be premature.¹¹

PREPARATIONS OF SPECIMENS

In this study of cold-work it was desirable to eliminate as far as possible all other

sources of internal friction. One disturbing source is the lack of temperature equilibrium between adjacent crystallites of a vibrating specimen.⁴ Temperature equilibrium is aided by small grain size and by the use of low-frequency vibrations. Unless unduly long specimens are used, low frequencies can be obtained only in transverse vibrations. But in transverse vibrations a second source of internal friction is present, that arising from transverse thermal currents.⁵ The effect of these may be reduced by increasing the transverse dimensions. The grain size and transverse dimensions of the specimens were thus so chosen as to render the vibrations simultaneously nearly isothermal with respect to intercrystalline thermal currents, and nearly adiabatic with respect to transverse thermal currents.

The material for this investigation was a 70-30 brass, part of the same lot of material that was used for some earlier studies on the effect of strain on proportional limit.¹⁰ It had the following composition: copper, 70.59 per cent; zinc, 29.39; lead, 0.01; iron, 0.01. This material was received from the brass mill in the form of $\frac{3}{4}$ -in. rod, cold-drawn to final size by a 65 per cent reduction of area from material that had been annealed to give a grain size of 0.060 mm. Rods of appropriate length were annealed for 2 hr. at 400°C. and cooled in air. The annealed rods (grain size, 0.012 mm.) were then stretched in a tension-testing machine, using special grips¹⁰ to ensure axial application of the load. The rate

This research was aided by grants from the Engineering Foundation, from the Penrose Fund of the American Philosophical Society, and from the Rumford Fund of the American Academy of Arts and Sciences. Manuscript received at the office of the Institute June 10, 1941. Issued as T.P. 1376 in METALS TECHNOLOGY, October 1941.

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† Research Metallurgist, American Brass Co., Waterbury, Connecticut.

¹ References are at the end of the paper.

of stretching was held constant at 0.05 in. per min. cross-head speed for samples 3 to 7, and was 12.5 times as rapid for samples 8 and 9. Strain was measured with a Ewing extensometer except in the sample extended 30 per cent, which was measured with dividers. The straining of the samples is summarized in Table I.

The strained specimens were cut to a standard length of 11 in. The diameter was 0.747 in. or less, depending on the reduction of area that accompanied the elongation during this process.

TABLE I.—*Straining of Samples*

Bar No. ^a	Maximum Applied Tensile Stress, Lb. per Sq. In.	Maximum Strain under Load, Per Cent	Residual Permanent Set, Per Cent	Internal Friction $1/Q \times 10^5$	Change in Internal Friction Due to Cold-work
E				Fig. 1, 3 Fig. 3	
B	13,720	1.1025	0.837		
2			0.000	0.35	
3	26,100	0.188	0.023	0.50	0.15
4	25,800	0.216	0.043	0.60	0.25
5	25,850	0.286	0.100	0.95	0.60
6	26,300	0.700	0.475	2.3	2.0
7	32,250	2.76	2.46	5.4	5.0
8	31,350	2.78	2.47	4.9	4.5
9	54,600	30.5	30.0	4.3	3.9

^a Samples E and B annealed 1 hr. at 400°C.; 2 to 9 annealed 2 hr. at 400°C. before straining, as shown.

EXPERIMENTAL PROCEDURE

The definition of internal friction used here, $1/Q$, is

$$\log_e n/\pi\tau_n f$$

Here f is the frequency of vibration, τ_n the time required for the amplitude of vibration to decay one n th of its initial value. The specific damping capacity, which is also a common measure of internal friction, is $2\pi/Q$.

The general method of supporting the specimens, of exciting and detecting the vibrations, has been described elsewhere.⁶ All measurements were made in a vacuum, as acoustical losses were found to raise the measured internal friction of some of the specimens as much as several fold.

The necessity of a vacuum introduced special difficulties at measurements above room temperature. In order that the wax joints on vacuum tank maintain a vacuum, it became necessary to solder near the joints copper tubing through which cold water was circulated. Naturally this formed considerable temperature gradients within the tank, so that it then became necessary, in order to determine the temperature of the specimen, to use some means for determining the temperature of the specimen itself during measurement rather than to consider the temperature of the specimen to be that of its surroundings. To do this, the silk threads used in previous experiments to support the specimen at its nodes of vibration were replaced by fine wires of the type used in making Chromel-Alumel thermocouples, one of the suspensions being of each metal. From these were brought heavier insulated leads of the same metals out through the vacuum tank to a cold junction, and to a means of measuring the electromotive force of the thermocouple. When the specimen was suspended in these supports, it then formed the hot junction of the couple, its temperature determining the couple's electromotive force.

MEASUREMENTS

Preliminary measurements were made on an unstrained specimen (sample E) in order to determine the frequency range in which the effects of thermal currents are a minimum. The observations are given in Fig. 1, and they are interpreted as follows:

The theoretical contribution of the transverse thermal currents to the internal friction is given very nearly by⁵

$$\text{Internal friction} = \frac{E_s - E_T}{E_T} \times \frac{f_0}{f_0^2 + f^2}$$

Here E_s and E_T are the adiabatic and isothermal Young's moduli, respectively, along the axis of the specimen, and f_0 is the frequency at which the internal friction is a maximum. The first factor is calculated

from the formula

$$(E_N - E_T)/E_T = TE_s\alpha^2/\rho C_p$$

where α is the linear thermal expansion co-

The theoretical value of the frequency f_0 is $2.16\sigma/\rho C_p d^2$. Here σ is the thermal conductivity, d the diameter. For our particular specimen this formula gives 0.20 cycles

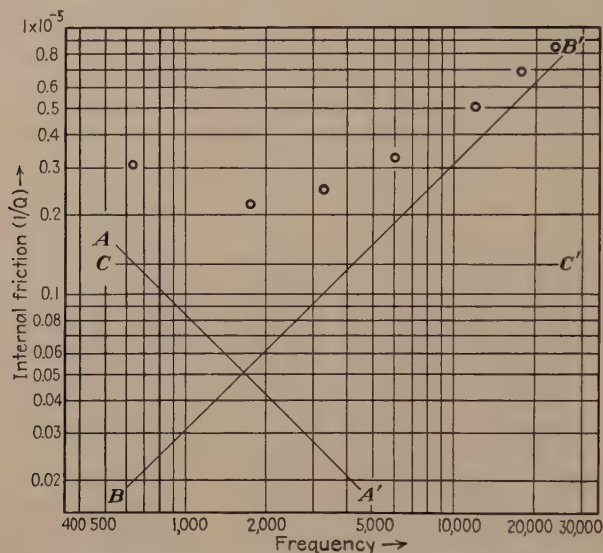


FIG. 1.—ANALYSIS OF INTERNAL FRICTION OF UNSTRAINED SPECIMEN.

To within experimental error, the internal friction may be expressed as the sum of three parts: AA' , due to transverse thermal currents; BB' , due to intercrystalline thermal currents; CC' , due to all other causes. The measurements at 6000 cycles per sec. and harmonics thereof were taken with longitudinal vibrations, at the lower frequencies with transverse vibrations.

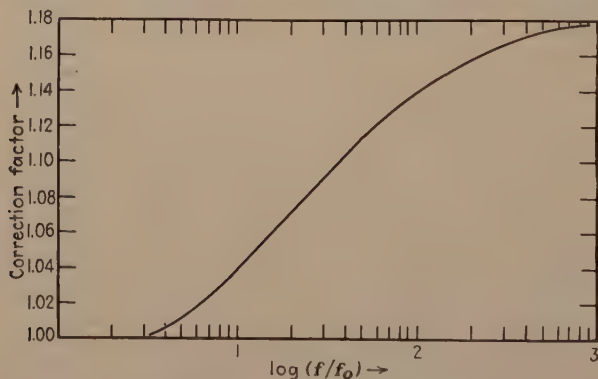


FIG. 2.—CORRECTION FACTOR FOR EQUATION 1.

efficient, ρ the density, C_p the specific heat at constant pressure. The modulus E_s of our particular specimen was measured from its resonance frequencies, and found to be 11×10^{11} dynes per sq. cm. Using this, the first factor obtained is 0.0035.

per sec. for f_0 . The right-hand side of Eq. 1, however, is only the first term of an infinite series. The percentage error made in neglecting the remaining terms is negligible only when f is less than or comparable to f_0 . The correction factor for large values of

the ratio f/f_0 has been calculated and is given in Fig. 2. In the frequency range here used it is 1.18. The contribution of the transverse thermal currents to the internal friction of this specimen, calculated in this manner, is $0.0085/f$ in the frequency range here used. This is represented by the straight line AA' in Fig. 1.

Theoretical considerations⁶ have shown that the contribution of the intercrystalline thermal currents to the internal friction is a linear function of the frequency f in the extreme isothermal range of this experiment. It will thus be represented by a straight line of slope unity in Fig. 1. The observations are consistent with the assumption that the contribution due to all other sources of internal friction is independent of frequency. This assumption gives BB' for the contribution of the intercrystalline thermal currents, CC' for the contribution due to all sources other than thermal currents.

In order to determine the frequency dependence of the internal friction introduced by cold-work, measurements were made over a wide frequency range on a specimen prepared in a manner identical to that used in obtaining Fig. 1, except for a final 0.84 per cent elongation (sample B). The measurements were made 15 months after the elongation. These are compared in Fig. 3 with those of the unstrained specimen. Within the limits of experimental error, the internal friction introduced by straining is seen to be independent of the frequency of measurement. This frequency independence definitely disproves an interpretation of the effect of cold-work advanced by one of us.⁷ It indicates that cold-work is associated with a hysteresis in quasistatic stress-strain measurements. This association of hysteresis with cold-work has been observed in single crystals.⁸

The specimens used in studying the effect of varying amount of cold-work are described in Table 1 together with the results obtained. All measurements were made at

the second resonance frequency for transverse vibration, of about 2000 cycles per sec., in order to minimize the effects of thermal currents. The measurements before

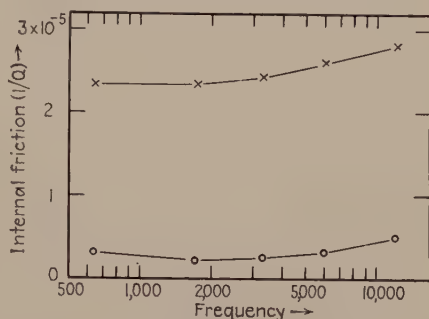


FIG. 3.—DEPENDENCE OF COLD-WORK INTERNAL FRICTION UPON FREQUENCY OF MEASUREMENT.

The o and x measurements were made before and after a 0.85 elongation, respectively. The difference is independent of frequency within experimental error.

annealing were made 16 days after the elongation. By comparing the observations for specimens Nos. 7 and 8, we see that the rate of straining has only a small effect upon the internal friction introduced by a given final elongation. In estimating the internal friction introduced by cold-working, we shall assume that this is added to the internal friction already present. This assumption is certainly invalid under most circumstances. Firstly, large strains are inevitably associated with a reduction in diameter, and hence with an increase in the effects of transverse thermal currents. Secondly, large strains are known to reduce⁹ the effects of intercrystalline thermal currents. However, by purposely making the effects of these thermal currents small, we have automatically rendered negligible the percentage of error introduced by such effects.

The internal friction introduced by cold-working, calculated in this manner, is given in Fig. 4 as a function of the percentage of elongation. The left-hand branch of this curve has a slope of unity, indicating that the internal friction introduced by cold-

work is proportional to the elongation, up to 0.1 per cent. A maximum is reached somewhere between 2.4 and 30 per cent.

Internal friction is a convenient and ex-

of us,¹⁰ undoubtedly is that the stress amplitude is so greatly different in the two cases.

The removal of the effect of cold-working

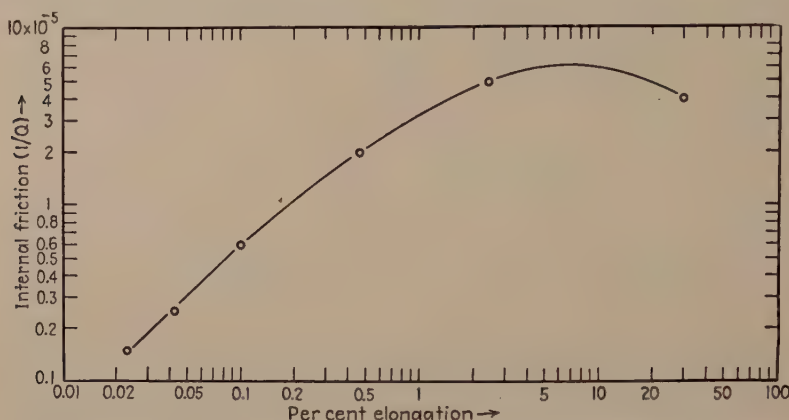


FIG. 4.—DEPENDENCE OF COLD-WORK INTERNAL FRICTION UPON PERCENTAGE OF ELONGATION. The slope of unity at left shows an initial linearity with percentage of elongation.

tremely sensitive measure of the area of a stress-strain loop, and hence would be expected to vary with the shape of this. The

by low-temperature annealing is illustrated in Fig. 5. The annealing was for 1 hr. in oil baths at 50°C., 100°, 150°, 200° and 225°.

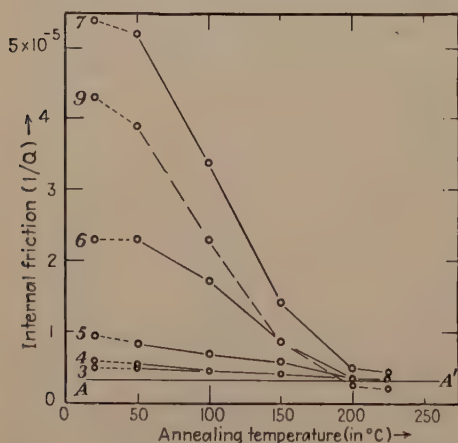


FIG. 5.—RELIEF OF COLD-WORK INTERNAL FRICTION BY ANNEALING.

Each anneal was for one hour. The horizontal line AA' represents the internal friction before elongation.

reason that there seems to be little correlation between the internal friction measured here and the changes in proportional limit induced by strain, recently studied by one

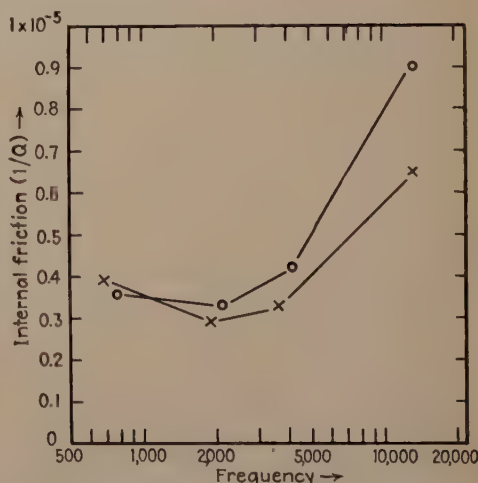


FIG. 6.—REDUCTION OF EFFECT OF INTERCRYSTALLINE THERMAL CURRENTS BY COLD-WORK.

The *o* are measurements before elongation, *x* after 30 per cent elongation followed by one-hour anneal at 200°C.

This annealing, including that at 225°C., caused no visible change of microstructure in any sample and no hardness change

greater than the experimental error of the Rockwell machine used. The anneal at room temperature does not properly belong upon these annealing curves, as this anneal was for 16 days. The specimen strained 30 per cent had an internal friction after the 200°C. anneal less than before straining. This may be attributed to the reduction of the intercrystalline thermal currents by cold-work, which has been mentioned. In order to test this interpretation, measurements were made over a frequency range on the 30 per cent elongated specimen after 200°C. anneal, and on the unstrained specimen (No. 2). These are compared in Fig. 6. The difference in the internal friction of the two specimens becomes greater as the frequency is increased; that is, as the intercrystalline thermal currents become relatively more important.

In studying the effect of the temperature of measurement, the strained specimen had first to be annealed at a temperature above the range over which measurements were to be made. Otherwise the specimen would change during measurement. The observations are shown in Fig. 7 on sample 8 after 1½-hr. anneal at 100°C. The variation with temperature of the internal friction introduced by strain is given by the difference between the observations on the strained specimen and on the unstrained specimen (sample 2), curve AA'. This is the only type of internal friction in non-ferromagnetics that has been found to decrease with an increase in temperature.

SUMMARY

1. The internal friction introduced by cold-working is independent of the frequency of measurement.

2. When the cold-work is introduced by stretching, the increase of internal friction is initially proportional to the elongation.

3. An optimum percentage of elongation exists, beyond which the internal friction decreases.

4. Annealing below the recrystallization temperature removes the internal friction introduced by cold-work.

5. The internal friction introduced by

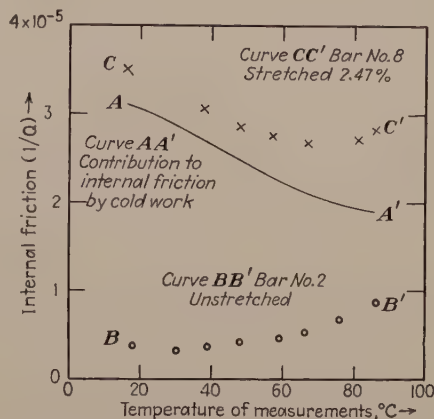


FIG. 7.—DEPENDENCE OF COLD-WORK INTERNAL FRICTION UPON TEMPERATURE OF MEASUREMENT.

The *o* are measurements before elongation (sample 2), the *x* are measurements after 2.4 elongation (sample 8) followed by 1½-hr. anneal at 100°C. Curve AA' is the difference between the two.

cold-work decreases with increasing temperature of measurement.

ACKNOWLEDGMENTS

The authors wish to acknowledge the advice and assistance of Mr. Donald Dilling in assembling the equipment for the measurements above room temperature.

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DISCUSSION

(*D. K. Crampton presiding*)

E. V. POTTER,* Salt Lake City, Utah.—The Metallurgical Division of the United States Bureau of Mines has done a considerable amount of work on the effect of cold-work upon the internal friction, or damping capacity, of a number of different metals and alloys. The internal friction was determined by a method closely related to that used by Dr. Zener and his co-workers and in every case the specimens were subjected to very small amplitude strains. The measurements were made using longitudinal vibrations at frequencies from 6 to 10,000 cycles per second, at room temperature.

In one series of experiments the specimens were cold-worked by subjecting them to torsional stresses above their elastic limit. The brass specimens showed an initial unstressed damping of 0.005 per cent, which increased with the degree of cold-working to 0.04 per cent, at which point 450 in.-lb. of work per inch of specimen had been put into the specimen. There was no indication that the damping would not continue to increase with additional cold-work, for the curve was still rising with a constant slope.

Our results showed three types of variations of damping capacity with the amount of cold-work. One group showed an increase in damping with cold-work. This type showed a nearly linear rise, or had an upward curvature. Examples of this were aluminum, brass, zinc and Armco iron. A second type showed a very rapid decrease in damping with small amounts of cold-work, say 50 to 100 in.-lb. per inch of length, after which very little change occurred up to as much as 1600 in.-lb. per inch. Examples of this type are copper, Permalloy and electrolytic iron. A third type is one combining the two; namely, an initial rise, which is quite rapid, followed by a fall in the damping, which is less rapid. This type is shown by manganese-copper alloys. Aging at room temperatures produced no changes greater than experimental error in any of these results.

In another series of experiments the specimens were subjected to tensile stresses up to

and exceeding the elastic limit. Curves were obtained for the manganese-copper alloys similar to those obtained by these authors for brass. In this case, however, the maximum damping occurred just before the specimen reached its elastic limit, about 45,000 lb. per sq. in. Since we do not have values for percentage extension, and the authors do not show values of stress corresponding to the various percentage extensions, we should like to know where the elastic limit for the brass specimens might be located on the curve.

Further work by the Bureau of Mines has been planned for this study, and after its completion a more complete report will be published.

G. SACHS,* Cleveland, Ohio.—Dr. Zener mentions that he is going to interpret this effect later on, in another paper. However, it appears that this is the fundamental effect, which we contribute to the so-called microscopic residual stresses in the metal. I do not know how the situation is at present regarding the correlation between microscopic and macroscopic stresses. It appears that they are fundamentally of the same nature and particularly should depend upon the temperature of anneal in the same way.

If internal friction is a direct measure of such stresses, it should be fairly simple to determine the magnitude as is done in this paper by means of a simple apparatus, and thus obtain the much desired data on the effect of relieving temperature on residual stress. The mechanical methods are complicated. It would, of course, simplify this problem tremendously if a little stress detector could be developed.

I have been wondering whether we can consider the internal friction actually as a measure for the magnitude of the microscopic residual stresses, and whether microscopic and macroscopic residual stresses are actually parallel regarding the effect of annealing temperature.

R. W. CARSON,† Little Falls, N. J.—We have been doing some internal stress measurement at the other end of the frequency scale, measuring the so-called drift under a single loading for long periods of time. Our time cycle is only

* Associate Electrical Engineer, U. S. Bureau of Mines. Discussion published by permission of the Director, Bureau of Mines, U. S. Department of the Interior.

* Associate Professor of Metallurgical Engineering, Case School of Applied Science.

† Development Director, Instrument Specialties Co.

half a load cycle, whereas these measurements have been made at very high frequencies.

We found that beryllium copper when heat-treated specifically for this low drift, or low internal friction condition, has far less internal friction than any other material we have had an opportunity to test. So, it certainly would be interesting to see how beryllium copper would work under these high-frequency tests.

C. ZENER, H. CLARKE AND C. S. SMITH (authors' reply).—Mr. Potter's observations clearly show that, at present, even the qualitative effect of cold-work upon internal friction is unpredictable in materials not previously examined. In some cases the internal friction is raised, in others it is lowered. This diversity no doubt is a reflection of the multiplicity of changes that cold-work introduces into metals. Thus the preferred orientation introduced by cold-work lowers the contribution of the

intercrystalline thermal currents to internal friction. Under appropriate conditions this one effect results in an actual lowering of the total internal friction by cold-work.⁹ The information requested by Mr. Potter concerning the stresses is given in Table 1.

The internal friction here studied has been interpreted¹¹ phenomenologically as a relaxation of stresses in localized regions rendered partially inelastic by cold-working. Dr. Sachs' suggestion that the internal friction is associated with microscopic stresses is not inconsistent with this interpretation. Regions of high localized stresses may very well behave inelastically with respect to superimposed uniform stresses. Experiments have not yet been performed to determine whether the relief of internal friction by annealing parallels the relief of macroscopic stresses.

High-temperature Internal Friction of Alpha Brass

By C. ZENER,* JUNIOR MEMBER A.I.M.E., D. VAN WINKLE† AND H. NIELSEN,*
MEMBER A.I.M.E.

(New York Meeting, February 1942)

THE internal friction of metals has been studied frequently at elevated temperatures.¹⁻⁴ In most cases it rises rapidly with increasing temperature. The notable exceptions are ferromagnetic materials, and lead.² This paper describes an investigation of the general features of the high-temperature internal friction of 70-30 alpha brass.

EXPERIMENTAL METHOD

The internal friction of a metal is a measure of the rate at which it dissipates energy of vibration. The measure adopted here, $1/Q$, is $(1/2\pi)$ times the specific damping capacity, a measure commonly used by engineers. In the measurements of this investigation, the stress level was kept so low that the observations were independent of the stress. The general method of making such measurements, and of observing temperature of a specimen during a measurement, has been described.^{5,6}

The driver and detector coils were wound with wire insulated with glass thread, in order to withstand the high temperatures used. In previous work electrical eddy currents in the specimen served as the coupling between the mechanical vibration of the specimen and the electrical circuits of the driver and detector. The high values of the internal friction in the present investigation rendered this coupling insufficient.

In order to increase this coupling, pole pieces cut from ordinary telephone diaphragms were attached to the specimen. A mixture of French chalk and water glass proved a satisfactory cement. All measurements were made at the fundamental frequency for transverse vibration, which lay between 600 and 900 cycles per second.

SPECIMENS

The measurements described herein were made upon a single cylindrical rod of brass, kindly furnished by Dr. Cyril Stanley Smith, of the American Brass Co. This rod was the specimen E of the set of alpha-brass rods described in an earlier paper.⁶ Successively larger grain sizes were obtained by annealing at successively higher temperatures.

A slice was cut off one end after each set of measurements. Grain counts were made on each slice by W. E. Lindlieff, of the American Brass Co. Nine fields were viewed on each piece, located as shown in Fig. 1. Results are given in Table 1. The grain size is defined in the usual way; namely,

$$\text{Grain size} = 1/n^{1/2}$$

where n is the mean number of grains per square millimeter.

EXPERIMENTAL RESULTS

This paper is concerned exclusively with the part of the internal friction that becomes dominant at high temperatures. It is thus desirable to separate this part of the internal friction from the part that is

This research was supported by a grant from the Engineering Foundation. Manuscript received at the office of the Institute July 20, 1941. Issued as T.P. 1404 in METALS TECHNOLOGY, January 1942.

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† Graduate Student in Physics, Washington State College.

¹ References are at the end of the paper.

dominant at room temperatures. This resolution will be the more perfect, the better we can guess the law of temperature variation of the two types of internal friction. At room temperature almost all the internal friction of annealed 70-30 alpha brass arises from thermal currents, which

H , called the heat of activation, is nearly independent of temperature and has a magnitude of the order of tens of thousands of calories per mol. We anticipate, there-

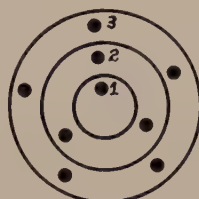


FIG. 1.—FIELDS FOR GRAIN COUNTS GIVEN IN TABLE I.

TABLE I.—Grain Counts of Specimens

Anneal, ^a Deg. C.	Magnifi- cation	Grain Count ^b			Grain Size, Mm.
		Location			
		1	2	3	
425	750	108	83 103 90	129 106 128 112 130	0.0089
500	750	38	39 34 42	33 29 41 43 39	0.0154
500	750 (repeat count)	41	36 40 33	31 33 33 34 38	0.0159
700	75	72	61 63 64	59 47 33 30 38	0.130
800	32	84	77 64 49	39 39 30 36 32	0.313
850	32	43	32 26 33	23 21 19 18 17	0.435

^a All anneals were for 2 hr., except the 850°C. anneal, which was for 13 hours.

^b Number of grains in area of 5000 sq. mm. at magnification stated.

inevitably accompany vibration.⁷ The theory⁸ of this effect predicts a very slow temperature dependence, at most a power dependence (T^n) with a small exponent ($n = 1$ or 2). On the other hand, the high-temperature internal friction presumably is due to some sort of plastic flow. Any ordinary theory of plastic flow (e.g., see Kauzmann⁹) leads to:

$$\text{Rate of plastic flow} \sim e^{-H/RT}$$

Here T is the absolute temperature, R the gas constant (1.986 cal. per deg. mol), and

fore, that in a plot on semilog paper of internal friction against $1/T$, the high-temperature component will be nearly a straight line with a quite steep slope, while the low-temperature component will vary only slowly with temperature. A typical set of measurements (after 700°C. anneal), is plotted in this way in Fig. 2. The observations may be represented as the sum of two components that vary in the manner discussed above.

The measurements after each anneal were plotted in the manner of Fig. 2. The measurements that lay upon the high-temperature branch, corresponding to branch CD of Fig. 2, are reproduced in Fig. 3. The low-temperature branch was lowest when the grain size was small; hence in Fig. 3 the measurements for the first anneals extend to a lower value of the internal friction than do those for the higher anneals.

DISCUSSION OF RESULTS

The most striking feature of these results is that, for any given temperature, the internal friction is smaller the higher the annealing temperature prior to measurement; i.e., the larger the grain size. This qualitative correlation of internal friction with grain size suggests that grain growth may be followed *during the anneal* by measurements on internal friction. Such

measurements have, in fact, been reported, although the observers were unaware of the significance of their observations. Thus Köster and Rosenthal (p. 1938, ref. 3) heated a specimen of cold-worked brass to 300°C. and recorded the variation of

with increasing temperature. From this slope may be calculated the heat of activation H , as defined by Eq. 1:

$$\frac{H}{R} = - \left\{ \frac{d}{d(1/T)} \right\} \log (\text{internal friction})$$

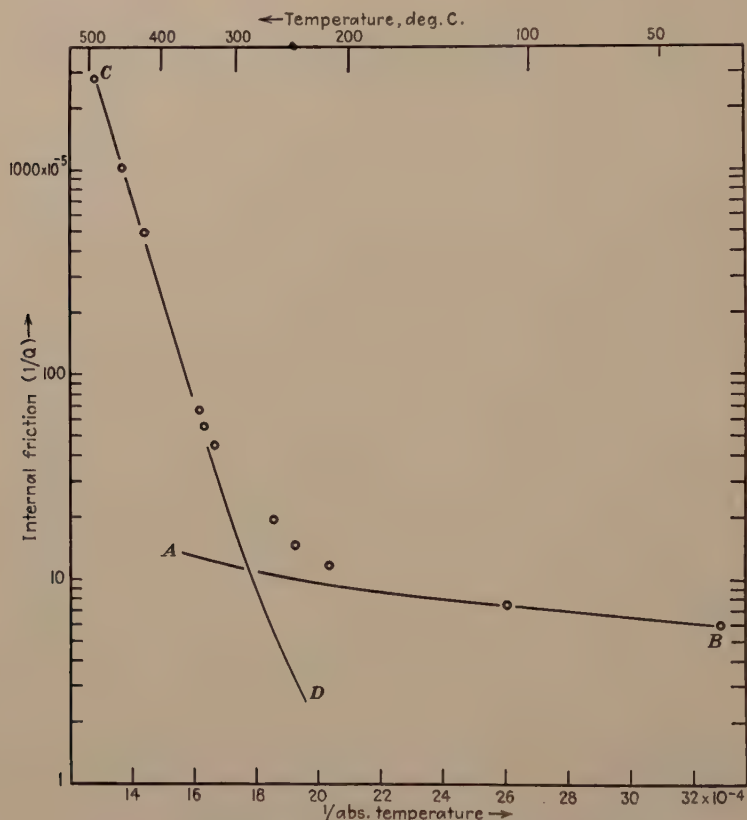


FIG. 2.—ILLUSTRATION OF METHOD OF PLOTTING OBSERVATIONS.

Total internal friction may be represented as the sum of two components, AB and CD , each of which is nearly a straight line. These data made after the 700°C. anneal.

internal friction with time at that temperature. They found it first increased then decreased slightly to a constant value. In the light of the present experiments, the initial increase was due to the formation of small grains upon recrystallization. As these grains grew, the internal friction was reduced.

Each set of data lies upon a nearly straight line, the slope of the line increasing

It ranges from 10,000 cal. per mol at the lowest temperatures to 20,000 cal. per mol at the highest temperatures. These values are considerably smaller than the heat of activation for the diffusion of zinc in brass; namely, 41,700.¹⁰ We conclude, therefore, that the internal friction observed here is connected in no way with atomic diffusion. Previous comparisons of the heat of activation for internal friction and for creep

with that for diffusion likewise give a factor of about 2. Thus in zinc the high-temperature internal friction has a heat of

others. It is thus to be expected that most of the variation between the various curves in Fig. 3 would be eliminated if proper

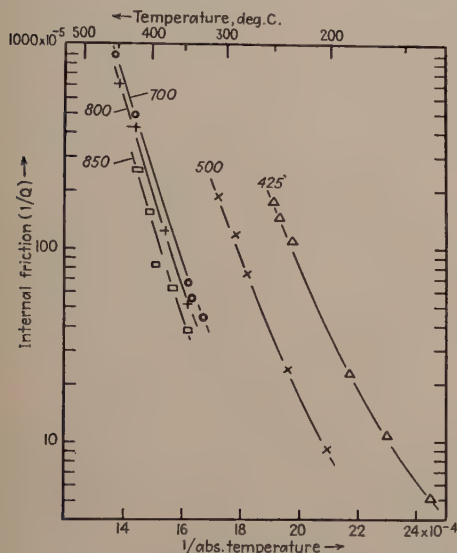


FIG. 3.—HIGH-TEMPERATURE INTERNAL FRICTION AFTER SUCCESSIVE ANNEALS.

Only observations that form the high-temperature branch of a curve, corresponding to CD of Fig. 1, are shown.

activation of 5200 cal. per mol.⁴ compared with 19,600 for self-diffusion in zinc.¹¹ The heat of activation for creep in lead is 16,500 cal. per mol, compared with 28,000 for self-diffusion.¹² The increase of the effective heat of activation with temperature is evidence that the results cannot be described by a single term of the form of Eq. 1, but rather by a summation of such terms with different H 's. That such a summation will necessarily lead to an increase of the apparent H with temperature is evident from Fig. 2. The superposition on semilog paper of two straight lines necessarily has a positive curvature.

The primary change in a recrystallized metal that occurs on annealing at successively higher temperatures is grain growth. Secondary effects are changes in grain-size distribution, changes in composition (de-zincification at high temperatures), and

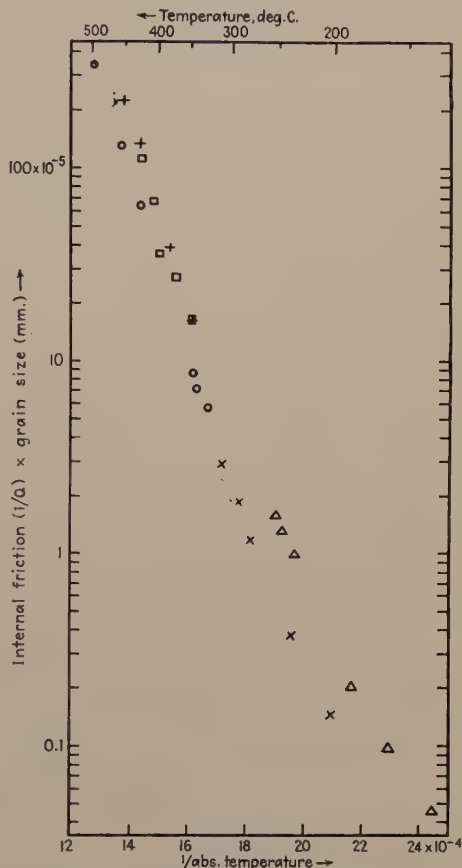


FIG. 4.—MEASUREMENTS OF FIG. 3 REPLOTED, THOSE FOR EACH ANNEAL BEING MULTIPLIED BY THE CORRESPONDING GRAIN SIZE.

account were taken of the change in grain size.

The total area of the grain boundaries per unit volume is proportional to the grain size, for the surface of a single grain has an area proportional to the square of its linear dimensions, while the number of grains per unit volume is inversely proportional to the cube of the linear dimensions of the average grain. Hence the total area is proportional to the first power of the

linear dimensions; e.g., to grain size as customarily defined. If the high-temperature internal friction is entirely a grain-boundary effect, such as slipping at boundaries, it will be inversely proportional to the grain size. If this were the case, the quantity (*internal friction*) \times (*grain size*) would be independent of grain size. In order to test this concept, all the observations of Fig. 3 are plotted in this manner in Fig. 4. All the observations except those for the extremely small grain size, obtained with the 425°C. anneal, lie fairly well upon a common curve.

The discrepancy for the specimen of smallest grain size suggests that some other factor than slipping at grain boundaries may be operating. One possibility lies in the mobility of the twin boundaries, which certainly move under conditions of normal grain growth, since the average width of twin bands is approximately a constant fraction of the grain size, irrespective of what this size may be. Under an applied stress these boundaries will move in such a direction as to relax the stress, and hence will contribute to the internal friction. It remains for future experiments to determine the order of magnitude of this effect.

The term "high temperature" is only a relative term, of course. Any reasonable extrapolation to room temperature of the curve in Fig. 4 for the original specimen gives a value greater than $1/Q = 0.1 \times 10^{-5}$. This bar has previously been found⁶ to have, under appropriate conditions, an internal friction of only 0.23×10^{-5} at room temperature. Hence in brass of small grain size the "high-temperature" internal friction is an important part of the total internal friction at room temperature.

SUMMARY

An investigation of the internal friction of 70-30 alpha brass at high temperatures has yielded the following results:

1. At high temperatures this internal friction is larger, the smaller the grain size.

The literature contains instances in which recrystallization and grain growth were manifested in the internal friction measured during the annealing treatment.

2. This internal friction depends upon temperature as if it were associated with a distribution of heats of activation, the maximum being about 20,000 cal. per mol. Comparison of this heat of activation with that for diffusion shows that this internal friction is in no way connected with atomic diffusion.

3. The observed dependence upon grain size indicates that this internal friction is due to internal surfaces. The present experiments cannot distinguish between the effects of a slip at the grain boundaries and of a movement of the twin faces.

4. This high-temperature internal friction, whatever its source, constitutes a large part of the total internal friction at room temperature in specimens having very small grain size.

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DISCUSSION

(Arthur Phillips presiding)

ARTHUR PHILLIPS,* New Haven, Conn.—I would like to ask Dr. Zener if he has had occasion to use aluminum, a metal that ordinarily does not twin, thereby obtaining data that may be associated with slip effects at grain boundaries only.

T. A. READ,† Philadelphia, Pa.—The correlation of the high-temperature internal friction of alpha brass with the grain size found by

* Professor of Metallurgy, Yale University.

† Frankford Arsenal.

Zener, van Winkle and Nielsen is a result of great importance. Since it is so important to the theory of the plastic properties of metals, I should like to suggest the desirability of obtaining more data. The results presented in this paper are based on measurements on a single specimen, annealed at successively higher temperatures.

It would be worth while to measure the internal friction of a series of specimens that have been cold-worked various amounts and then annealed at such temperatures that the final grain sizes are the same.

C. ZENER, D. VAN WINKLE, H. NIELSEN (authors' reply).—Professor Phillips' suggestion to investigate aluminum at high temperatures is excellent. In aluminum the disturbing effect of intercrystalline thermal currents is much less, about one tenth less, than in alpha brass.¹³

The authors sympathize with Dr. Read's desire for more data. This is especially true because the concept of slipping at grain boundaries is repugnant to some metallurgists.

¹³ *Phys. Rev.* (1940) **58**, 472.

Diffusion of Zinc in Alpha Brass

By E. O. KIRKENDALL,* JUNIOR MEMBER A.I.M.E.

(New York Meeting, February 1942)

THE investigation reported herein was undertaken to obtain data to supplement those presented in an earlier paper,¹ particularly for longer times at a higher temperature. This information may further develop our knowledge of the mechanism of diffusion in substitutional solid solutions.

Diffusion of solute atoms interstitially dissolved is not difficult to visualize; it can take place without much disturbance of the solvent atoms. The mechanism of diffusion of solute atoms substitutionally dissolved is not so easily understood. Many theories have been advanced. Rosenhain,^{2,3} Frenkel,⁴ Smekal,⁵ Langmuir,^{3,6} Steigman, Shockley and Nix,⁷ and Johnson⁸ all proposed theories to explain diffusion.

Langmuir's proposed mechanism consisted of a simple cyclic interchange of atoms involving an interchange in lattice positions of four or more atoms. This mechanism, accepted by the author at the time of his previous publication,¹ and apparently quite generally accepted, required a net exchange in positions of both solute and solvent atoms in equal numbers. In other words, the rate of diffusion of the solvent and solute atoms would be the same. That this cyclic interchange in lattice positions of solute and solvent atoms in equal numbers is the only true mechanism of diffusion is denied by the evidence presented in this paper.

EXPERIMENTAL PROCEDURE

This modification of similar procedure¹ will be outlined briefly. The method consisted of the following steps:

1. A pure Muntz metal (60.6 per cent Cu, 0.1 per cent total impurities) that was almost all beta brass at 780°C. was chosen.

2. The brass was turned between centers in a lathe to a diameter of 0.5965 inches.

3. After the brass was cleaned, it was electroplated with pure copper to a diameter of about one inch.

4. The sample was heated slowly to 400°C. under reduced pressure and held at that temperature for 4 hr. to remove occluded gases. It was then cooled to room temperature.

5. The sample was heated to 780°C. $\pm 3^\circ\text{C}$. and held at that temperature for different lengths of time; then quenched. Samples were cut off each time after quenching. Metallographic samples $\frac{1}{4}$ in. thick were removed at 1 hr., 6 hr., 24 hr., 96 hr. and 701 hr. After 96 and 701 hr. samples of about 1 in. were removed for X-ray analysis.

6. The metallographic samples were polished on the cross section and photomicrographs were taken.

7. The 1-in. samples were polished and etched on both ends. With the aid of a microscope each was carefully mounted in a four-jaw chuck in a lathe, so that they could be accurately bored for an arbor.

8. Turnings were taken for each X-ray sample. After each set of turnings, the sample was heated in an oil bath for about $\frac{1}{2}$ hr. at 300°C. It was then etched in 25

Manuscript received at the office of the Institute Aug. 29, 1941. Issued as T.P. 1431 in METALS TECHNOLOGY, February 1942.

* Instructor, College of Engineering, Wayne University, Detroit, Mich.

¹ References are at the end of the paper.

per cent nitric acid, to clean the surface, and, using pure gold powder on the surface as a known, a back-reflection X-ray diffraction picture was taken of the surface.

measured directly on the ground glass of the microscope camera at 50 diameters. The Ames dial gauge attached to the stage when the microscope was set up for 50

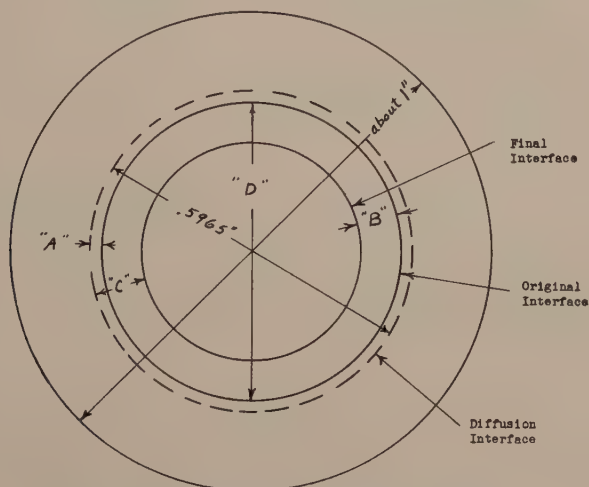


FIG. 1.—CROSS SECTION OF DIFFUSION SAMPLE.

The final interface is between the beta brass and the alpha brass.

The original interface is the outer boundary of the columnar grain area or the microscopic evidences of the original beta brass-copper interface. The diffusion interface is the actual location of the original beta brass-copper interface and is used in making calculations, since the composition of the alpha brass does not change at this point. It is not an arbitrary interface established to meet the needs of a differential equation.

In order to determine how much the original interface shifted from its original position, the polished and etched samples

diameters gave more accurate results than measuring directly at a very low magnification for the diameter measurement. *A* and *C* were then calculated from these measurements.

TABLE I.—Extent of Diffusion at 780°C.

Time, Hr.	Distance between Original and Final Interfaces (<i>B</i> , Fig. 1), In.	Shift in Original Interface (<i>A</i> , Fig. 1), In.	Total Extent of Diffusion (<i>C</i> , Fig. 1), In.
1	0.0030	0.0007	0.0037
6	0.0073	0.0014	0.0087
24	0.0142	0.0026	0.0168
96	0.0289	0.0040	0.0329
701	0.0812	0.0098	0.0910

RESULTS

Figs. 2 to 7 show the photomicrographs taken at 50 diameters. The samples were etched with a mixture of hydrogen peroxide and ammonium hydroxide. Two photomicrographs of the 701-hr. sample are included to show the uniformity of diffusion. An alpha-brass layer is formed on each side of the original interface. The alpha layer inside of the original interface is composed of large columnar grains with a definite final interface caused by the change in phase. The higher-copper alpha-brass layer outside the original interface shows neither a change in grain shape nor a definite final

were placed on the stage of a large microscope. An Ames dial gauge was attached to the stage of the microscope and readings were taken at opposite ends of the diameter (*D* in Fig. 1) of the original interface boundary. The distance between original and final interfaces (*B* in Fig. 1) could be



FIGS. 2-7.—DISTANCES BETWEEN INTERFACES.
Original magnification 50 \times reduced $\frac{1}{2}$ in reproduction.

interface, since copper and alpha brass have the same atomic arrangement. The data for the diffusion-penetration curves are given in Tables 1 and 2. Figs. 8 and 9 show the data plotted. The data necessary for calculating the rates of diffusion were taken from Fig. 9 and the results are given in Table 3.

TABLE 2.—X-ray Data

Distance from Diffusion Inter- face, In.	Lattice Constant, Å.	Zinc, Per Cent
FOR 96-HOUR SAMPLE		
+0.017	3.608	0.0
+0.012	3.613	2.5
+0.006	3.647	18.5
-0.001	3.667	27.5
-0.007	3.675	30.5
-0.013	3.679	32.0
-0.020	3.683	33.5
-0.026	3.685	34.5
FOR 701-HOUR SAMPLE		
+0.040	3.607	0.0
+0.031	3.613	2.5
+0.022	3.638	14.5
+0.012	3.645	17.5
+0.002	3.663	25.5
-0.009	3.668	28.0
-0.019	3.671	29.0
-0.030	3.673	29.5
-0.039	3.676	31.0
-0.051	3.679	32.0
-0.064	3.682	33.5
-0.079	3.682	33.5

area A . D is the diffusion coefficient. Its calculation was accomplished by rewriting Fick's law and using unit area and increments instead of differentials, as follows:

$$D = \Delta m / (\text{average } dc/dx) \Delta t$$

The data necessary to solve this equation are given in Fig. 9 and Table 3. From these D can be calculated and an average D of 3.8×10^{-9} sq. cm. per sec. at 780°C . for a 26 per cent Zn brass results.

The determination of a diffusion coefficient, however, is not the most important development from this work. It has already been mentioned that the location of the original interface shifts. This can be accounted for to a small extent by the fact that the beta brass changes to a denser, higher-copper alpha brass. In itself, this shrinkage in volume would account for less than one fifth of the shift in position of the original interface.

In order to explain the rest of the shift in the original interface, the author proposes that the zinc diffuses more rapidly than the copper in alpha brass. The diffusing out of the zinc faster than the copper can diffuse in necessitates a reform-

TABLE 3.—Calculation of Diffusion Coefficient

Time, hr.....	1	6	24	96	701
m , cu. in.....	0.00037	0.00086	0.00166	0.00326	0.00886
dc/dx , per cent per in.....	8000	3400	1760	900	260
Δm , cu. in.....	0.00049	0.00080	0.00160	0.00560	
Average dc/dx , per cent per in.....	4500	2400	1220	420	
Δt , hr.....	5	18	72	605	
D , sq. cm. per sec. $\times 10^{-9}$	3.9	3.3	3.3	3.9	

DISCUSSION OF RESULTS

The quantitative treatment of diffusion in solid metals is based on Fick's law:

$$dm = -DA(dc/dx)dt$$

when dm is the amount of matter diffusing in time dt in the direction of a concentration gradient $-dc/dx$ and across an

ing of the lattice (without destroying the columnar grain structure in this case). The reformation of the lattice without some of the zinc atoms causes a contraction and a shift in position of the original interface in the direction of the high-zinc brass. This is well shown in Figs. 2 to 7. In other words, instead of an equal interchange of solute and solvent atoms during diffusion,

some of the solute atoms presumably diffuse out individually, while the body of the metal (solvent and solute atoms) moves in the direction of the high-zinc side to take

equal to the sum of two items: (1) The zinc that, having diffused across the diffusion interface, is measured by the included area to the right of the diffusion interface in

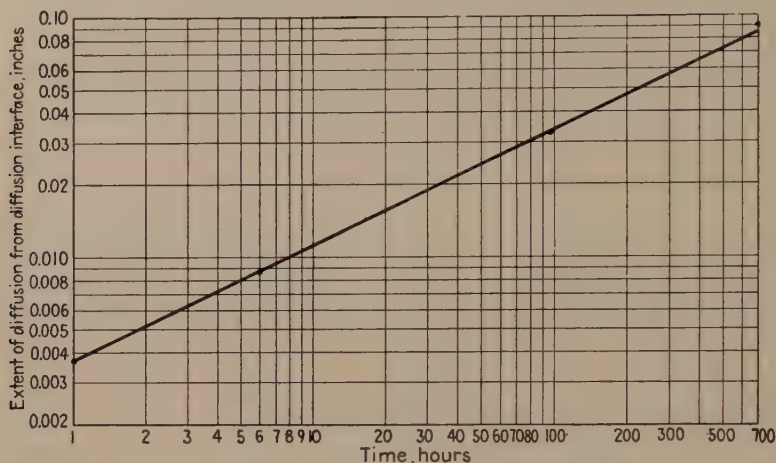


FIG. 8.—EFFECT OF TIME ON EXTENT OF DIFFUSION.

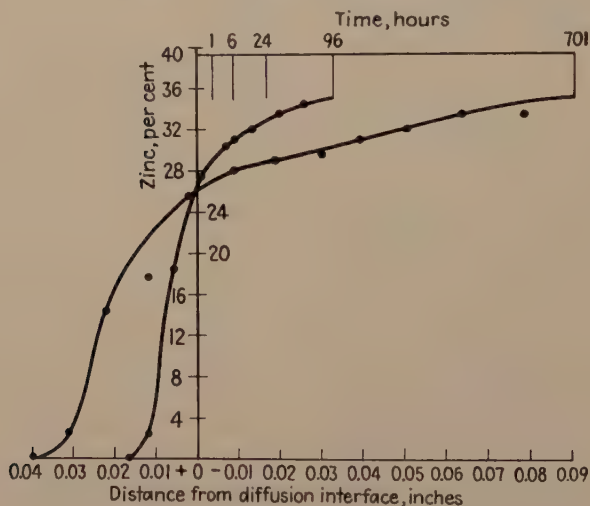


FIG. 9.—DIFFUSION CURVES AT 780°C.

up the space provided by the contraction of the high-zinc solid solution when the zinc diffuses out.

In calculating the rate of diffusion, two or three steps may not be obvious. The amount of zinc diffusing across the diffusion interface, at the position of the copper-beta brass interface before diffusion, is

Fig. 9. A correction to compensate for the fact that the interface was a cylinder and not a plane, was carefully made. (2) The zinc that, because of the mass movement of the alpha brass to take the place of the zinc, was carried across the diffusion interface, and subsequently diffused out. This additional amount of zinc is equal to the

composition of the alpha brass at the diffusion interface (26 per cent Zn) multiplied by the density of the brass and the amount of shift in the position of the original interface.

Since the shift in the original interface was not known at the time of the first publication, the diffusion coefficient given here for 780°C. cannot be exactly correlated with those of the previous publication. Likewise, the rate of diffusion for zinc in alpha brass given here cannot be correlated with most other published data. Most of the coefficients published were calculated by using the assumption of equal interchange of solute and solvent atoms.

SUMMARY

Evidence has been presented to indicate that, in at least one example of a substitutional solid solution (alpha brass), diffusion of solute and solvent atoms can proceed independently of each other at different rates. A diffusion coefficient of 3.8×10^{-9} sq. cm. per sec. for zinc in a 26 per cent Zn alpha brass was determined at 780°C.

ACKNOWLEDGMENT

The author wishes to express his appreciation in particular to George Reed for preparing the sample for the diffusion treatment and to thank the staff and assistants at Wayne University who helped build the X-ray diffraction equipment used on this research. Thanks are due also to Professor Upthegrove and Dr. James Freeman, of the University of Michigan, for suggestions and criticisms in preparation of this paper.

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DISCUSSION

(M. A. Hunter presiding)

M. R. HERMAN,* Dahlgren, Va.—I performed a series of experiments on the diffusion of aluminum in alpha aluminum bronze at the University of Michigan, with Prof. Clair Upthegrove. The phenomena observed during this investigation are in complete qualitative agreement with the results of the work on zinc-copper alloys investigated by Dr. Kirkendall and presented in the paper under discussion.

Without any knowledge of the unusual migration observed by Dr. Kirkendall, I noted a distinct discrepancy in the computations of the so-called "master curves" in the work on aluminum bronze. This curve is a useful tool in combining the diffusion curves for various lengths of time into one curve, which is then characteristic of the diffusion of that alloy at the given temperature. In order that this curve shall be accurate, it had been supposed that the areas under the two sides of the curve (representing, respectively, the diffusion of copper and aluminum atoms) must be equal in order to conform to substitutional diffusion. These areas turned out to be unequal, yet the various curves still fitted a master curve. This indicated a definite quantitative discrepancy amounting to several per cent of the total diffusion.

I was unable to account for this irregularity until a conference with Dr. Kirkendall revealed that he had been confronted with the same thing in his work. At that time Dr. Kirkendall suggested the possibility of interface migration and its cause. Following that conference the procedure was altered somewhat in order to measure the migration in aluminum bronze, if it did exist.

The aluminum-copper system is very similar to the zinc-copper system and it was found that the former does show a definite interfacial

* Ensign, Ordnance, United States Naval Reserve, U. S. Naval Proving Ground. The contents of this discussion in no way reflect the opinions of the United States Navy nor any of its official sources of information. (By General. Ord., U.S.N.)

migration. At 931°C. with a composition of 9.48 per cent Al in the base metal, and 5.83 per cent Al at the final position of the diffusion interface, the migration observed was about 11 per cent of the total penetration. Likewise at 846°C., with a base metal composition of 10.03 per cent and a diffusion interface composition of 6.24 per cent, the migration observed was about 7.5 per cent of the total penetration. This is in the same order of magnitude observed by Dr. Kirkendall in his investigation; i.e., 11.4 per cent.

When these corrections were incorporated into the calculations, the results corroborated data observed by Rhines and Mehl,⁹ who used a method that did not involve the use of an interface reference plane.

While this confirms the claim that interface migration exists, more quantitative data are necessary in order to form an exact opinion as to its cause.

E. A. ANDERSON,† Palmerton, Pa.—Dr. Kirkendall's paper, surprisingly enough, does include, although I do not think he quite realizes it, a very interesting practical application of the co-diffusion of zinc and copper. In the copperplating of zinc, blistering is frequently observed, blisters always breaking

loose in the diffusion zone between the copper and the zinc, with a very definite migration from the original interface between the copper electrically deposited and the zinc surface.

If Dr. Kirkendall would like to extend his work further in a very practical field, I can offer him two problems, or two questions to answer:

1. Why do copper and zinc interdiffuse more rapidly when the zinc surface on which the copper is deposited is unworked than they do when the zinc surface is worked to the extent of the normal buffing operation?

2. Why does the rate of diffusion in the diffusion of copper and zinc increase in direct proportion to the length of time of alkaline cleaning prior to plating?

Those two things have been observed and repeated by several laboratories. We need an explanation, which is tied up in some way with this whole diffusion phenomenon.

E. O. KIRKENDALL (author's reply).—The problems suggested by Mr. Anderson are more involved than they appear. Besides the effects of buffing and cleaning on the amount of diffusion, the measurement of the amount of diffusion is complicated by the fact that diffusion in such experiments is taking place in five solid solutions simultaneously. The two problems would make very interesting laboratory research work.

⁹ F. N. Rhines and R. F. Mehl: *Trans. A.I.M.E.* (1938) **129**, 185.

† Chief of Metal Section, Research Division, The New Jersey Zinc Co.

Magnetic Studies on the Precipitation of Iron in Alpha and Beta Brass

BY CYRIL STANLEY SMITH,* MEMBER A.I.M.E.

(New York Meeting, February 1942)

ON the 6th of February 1684, Dr. Martin Lister mentioned at a meeting of the Royal Society¹ that "brass is magnetical," and promised to give an account of that assertion at some other time. He repeated his promise but never fulfilled it, and it was left for William Arderon² to show, in 1758, that brass could be made magnetic by hammering and that it would retain polarity after magnetizing. Twenty-seven years later Cavallo^{3,4} examined the matter in great detail. Working with cast calamine brass, he showed that it could be made magnetic by hammering and nonmagnetic by subsequent annealing at a red heat. He found that annealing at a very high temperature caused the samples to lose their magnetic quality permanently, even after subsequent cold-working, but that remelting and cold-working restored it. He encountered some samples of brass that could not be rendered magnetic by any treatment. Experiments in which these were remelted with iron additions gave negative results, and Cavallo concluded that iron impurity was not the cause of the magnetism. He worked with 50-grain (3-gram) samples melted under the blowpipe, hence cooled very quickly. Bennet⁵ made whole crucible charges from copper and zinc, and found the resulting brass ingots to be magnetic only when iron had been added and then only after cold-working. All these observations applied to material in the cast condi-

tion, in which coring would produce a continuous spectrum of composition and cooling would result in varying degrees of precipitation.

This knowledge of the subject seems to have been forgotten in the nineteenth century. The older brass was made by the calamine process and frequently contained iron in amounts of 0.5 per cent or more, absorbed from the impure ore with which the copper and charcoal were heated in making the brass. When metallic zinc became available in commercial quantities, calamine brass gradually disappeared, and with it the knowledge of its curious magnetic properties. Only when sensitive apparatus replaced the compass needle of the earlier investigators could the effects be detected in relatively pure metal.

The effect of cold-working in inducing ferromagnetism was rediscovered by Bitter⁸ in 1930 in a sample of impure copper, and this was confirmed by Lowance and Constant,⁹ Honda and Shimizu,^{10,11} and others. In the same year, Tammann and Oelsen¹² showed that copper-rich copper-iron alloys after certain heat-treatments could be rendered ferromagnetic or made more strongly ferromagnetic by cold-rolling. Kussman and Seeman¹³ showed that the change of susceptibility of relatively pure copper on cold-working was associated with the iron content, and concluded that actual precipitation of iron was caused by cold-working, which is a satisfactory theory until one considers the improbably high rate of diffusion that this would involve. When studying precipitation phenomena in

Manuscript received at the office of the Institute July 7, 1941. Issued as T.P. 1394 in METALS TECHNOLOGY, December 1941.

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¹ References are at the end of the paper.

an alloy of copper with 2.4 per cent iron, Gordon and Cohen¹⁴ showed that a non-magnetic precipitate appears far in advance of magnetic precipitation of iron, and the

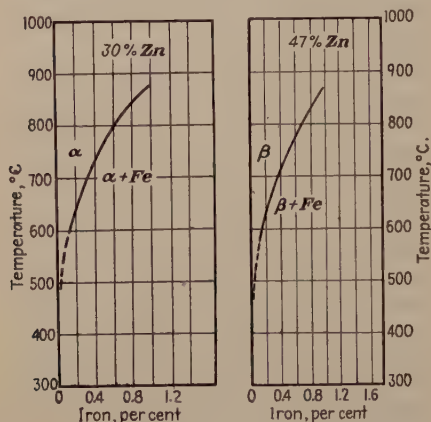


FIG. 1.—SOLUBILITY OF IRON IN ALPHA AND BETA BRASS. (BAUER AND HANSEN.²⁰)

present writer¹⁵ has shown that cold-working at this stage produces strong ferromagnetism and detectable body-centered-cubic lines in the X-ray diffraction pattern. It seems probable that the first precipitate is face-centered cubic in structure like the mother lattice, and that this is relatively stable in the absence of cold-work. Bitter and Kaufmann¹⁶ reached a similar conclusion as a result of measurements of susceptibility at high field strengths during precipitation and after cold-work. The recent results of Constant and his coworkers¹⁷ lend further support to this theory.

Under certain conditions of heat-treatment, therefore, iron will precipitate from solid solution in copper—and, presumably, many of its alpha alloys—in a nonmagnetic form that can be converted to a magnetic form by simple cold-working.* Both a double thermal treatment to produce the precipitate and subsequent plastic deformation to cause it to change to a magnetic form are necessary, and the divergence of published experimental result and opinion

* The term "magnetic" will be used in this paper as meaning ferromagnetic.

is hardly surprising. The present investigation was initiated in an effort to understand the curious behavior of a sample of commercial brass intended for instrument construction, but includes some experiments directed toward an understanding of the precipitation process.

Some attempts^{6,7} to use magnetic methods for the determination of the iron content of brass have failed to give useful results, which is to be expected in view of the enormous effect of prior thermal and mechanical treatment on the magnetic properties of brass of a given iron content.

The relevant portion of the copper-zinc-iron constitution diagram has been determined by Bauer and Hansen,²⁰ from whose work have been taken the solubility curves of iron in alpha and beta brass shown in Fig. 1. Magnetic and other studies by the writer are in close agreement with these.

APPARATUS AND METHODS

The brasses used in this investigation were made with various amounts of iron but the zinc was held constant at 30.0 per cent in the alpha series, 47.0 per cent in the beta alloys. They were made by melting in clay-graphite crucibles, in an induction furnace, the appropriate amounts of cathode copper, selected Grade 1A electrolytic zinc, and Armco iron. Great care was taken to obtain uniformity of composition. The melt was kept covered with charcoal and was poured through a copious gas flame to avoid oxidation. The castings measured $\frac{5}{8}$ by $1\frac{1}{4}$ by 5 in. and were hot-rolled to a thickness of 0.3 in. and cold-rolled to 0.04 in., with intermediate annealing at 800°C. at 0.160 and 0.080-in. gauge. All anneals were done in air in an automatically controlled electric furnace. The beta brass alloys which, of course, could not be cold-rolled, were hot-rolled in two stages to 0.040 in. Rolling was done between steel rolls, 5 in. in diameter, carefully cleaned to avoid contamination and liberally oiled. The samples for magnetic measurement

were usually $\frac{3}{4}$ in. square and 0.04 in. thick before cold-rolling; 0.02 in. after rolling. They were pickled in nitric acid before measurement. Shearing and numbering was done before heat-treatment, to avoid strain.

Remanence (residual magnetic moment) was chosen as the simplest of magnetic properties to determine. The samples were first saturated by being placed in the field of an electromagnet producing a field strength of about 7000 gauss in a gap 3 cm. in diameter and 2 cm. long. The residual magnetization was determined by observing the deflection of the sample suspended on a fine bronze wire in the center of a Holmholtz pair of coils. Field strengths of 1 to 10 gauss were applied and reversed readings were taken to eliminate deflection due to the susceptibility and shape of the sample. A deflection corresponding to a remanence of 10^{-5} could be seen. The apparatus is essentially that of Bitter, described by Constant and Formwalt¹⁸ and Gordon and Cohen.¹⁴ Each sample was weighed and the results are reported as remanence per gram; specific remanence may be obtained by multiplying this figure by the density (8.51 for 30 per cent Zn; 8.25 for 47 per cent Zn).

Remanence is greatly affected by the shape and size of the magnetic particles concerned. Undoubtedly it would be preferable to determine magnetic susceptibility over a wide range of field strengths, but such measurements require elaborate apparatus and are time consuming. For preliminary studies on a wide range of samples the method of determining remanence has great advantages.

EFFECT OF COLD-ROLLING UPON REMANENCE

Fig. 2 shows the effect of progressive cold-rolling on the remanence of 70-30 brass containing 0.053 and 0.100 per cent Fe, previously quenched from 800°C. and reheated for 135 hr. at 450°C. to produce a

copious but nonmagnetic precipitate. The remanence, initially very low in the reheated condition, increases continuously with increasing cold-work. In curves A and

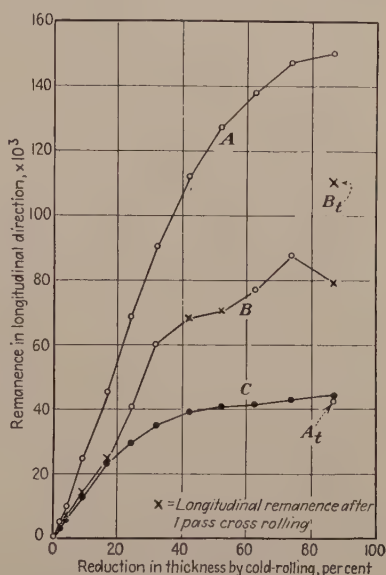


FIG. 2.—EFFECT OF COLD-ROLLING ON REMANENCE OF ALPHA BRASS.

30 per cent Zn, 0.100 per cent Fe (curves A and B), and 0.053 per cent Fe (curve C), previously quenched from 850°C. and annealed 135 hr. at 450°C.

Measurements in direction of original rolling except points marked A_t and B_t .

C the remanence was measured after magnetizing in the same direction as that in which the piece had been elongated by rolling. It was much less when measured transversely in a severely rolled sample, as shown by the point A_t in Fig. 2, which is the terminal sample of curve A magnetized at 90° to the rolling direction. The effect probably is due to the elongated shapes of the particles, though it may be an orientation effect. In one sample (curve B, Fig. 2) the piece was turned through 90° and cross-rolled after every two or three passes, producing less difference between the two directions. Point B_t is the remanence transverse to the original rolling direction but actually in the direction of greatest elonga-

tion. In the work described below, heat-treatment was followed by a standard reduction of 50 per cent in thickness, produced by rolling in three passes, and the

PRECIPITATION OF IRON FROM DILUTE SOLUTION IN ALPHA BRASS

Alpha brass containing iron in solid solution possesses no measurable remanence

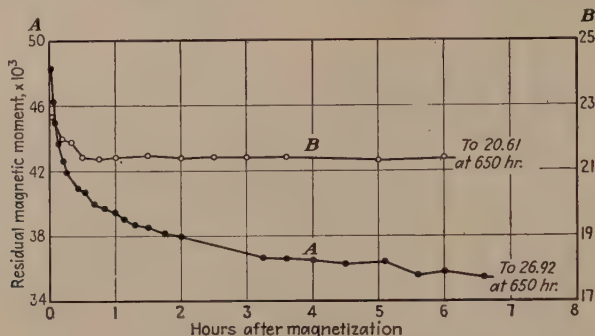


FIG. 3.—CHANGE OF REMANENCE WITH LAPSED TIME AFTER MAGNETIZATION.

Curve A = 30 per cent Zn, 0.153 per cent Fe, quenched from 900°C., reheated 32 hr. at 450°C. and cold-rolled 50 per cent.

Curve B = 30 per cent Zn, 1.025 per cent Fe, quenched from 800°C., reheated 32 hr. at 450°C., not cold-worked.

sample was magnetized in the same direction as it was rolled.

In common with most ferromagnetic materials, the residual magnetism slowly decreased with time (Fig. 3). The change is

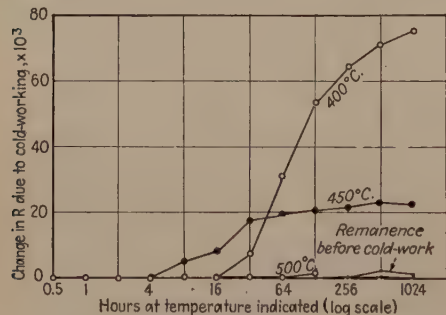


FIG. 4.—EFFECT OF REHEATING TIME AT VARIOUS TEMPERATURES ON SUBSEQUENT CHANGE OF REMANENCE ON COLD-ROLLING.

70-30 brass containing 0.053 per cent Fe quenched from 800°C. before reheating at 400°, 450° or 500°C.

greater in the samples made ferromagnetic by cold-working (curve A) than in those containing free ferritic iron on heat-treatment alone (curve B). An "aging" period of 1.5 ± 0.5 hr. was arbitrarily adopted for all measurements.

when quenched and it does not become magnetic on cold-rolling to any degree. If, however, it is reheated for a long enough time at a temperature at which the iron essays to come out of solution, then, though the alloy will be barely perceptibly magnetic in the reheated condition, it will become strongly magnetic on subsequent cold-working. The effect of various conditions of reheating is shown for alloys with 30 per cent Zn and 0.053 and 0.100 per cent Fe, respectively, in Figs. 4 and 5. The samples, 0.040 in. thick, were quenched after 1 hr. at 800°C. and reheated for the times shown at 400°, 450° and 500°C. Remanence was measured before and after cold-rolling to a reduction of 50 per cent. In the quenched condition the samples were completely nonmagnetic. There was a slow and slight increase in remanence on reheating, but the greatest change came after cold-working. This indicates that there is a very small amount of magnetic precipitate formed, presumably at the grain boundaries, by reheating alone, but the bulk of the precipitate (or zone, knot or other transitional structure responsible for the

effects) is nonmagnetic and is revealed only after plastic deformation. Except for the anomalously low rate of the 0.10 per cent Fe alloy at 400°C., the rate and extent of

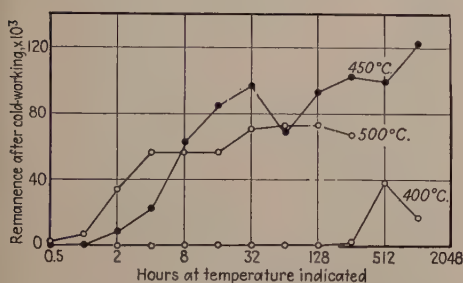


FIG. 5.—EFFECT OF REHEATING TIME AT VARIOUS TEMPERATURES ON SUBSEQUENT CHANGE OF REMANENCE ON COLD-ROLLING.

70-30 brass containing 0.100 per cent Fe, quenched from 800°C. before reheating at 400°, 450° or 500°C.

precipitation is exactly what would be expected from the solubility relations concerned.

These results were obtained on alloys quenched from 800°C. If the samples were quenched from lower temperatures before reheating, precipitation of the trace of directly magnetic material was the same as before, but the rate of precipitation of the bulk of the iron, magnetically detectable only after rolling, is very much less than after the quench at the higher temperature. This astonishing result is shown in Fig. 6, which shows the 0.053 per cent Fe alloy of Fig. 4 reheated at 450°C. after three different treatments: (1) quenched after 1 hr. at 800°C.,* (2) furnace-cooled in 1 hr. from 800° to 600°C., held 1 hr. and quenched, and (3) treated with specimens in treatment 2 and further furnace-cooled in 2 hr. to 400°C., held 1 hr. and quenched. There was a small amount of direct magnetic precipitation at 450°C. prior to cold-work, reaching a maximum of about

2×10^{-3} in 512 hr. This was the same in all samples, regardless of quenching temperature. It is obvious from Fig. 6 that prior treatment, *even in the solid solution*

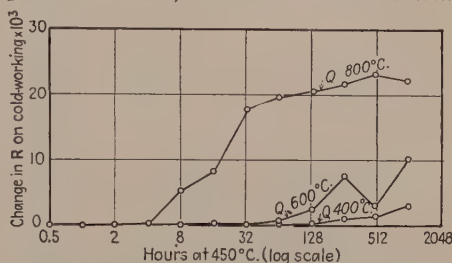


FIG. 6.—EFFECT OF REHEATING ON SUBSEQUENT CHANGE OF REMANENCE ON COLD-ROLLING.

70-30 brass containing 0.053 per cent Fe, quenched from 800°, 600° or 400°C. before reheating at 450°C. for times shown.

range, has a great effect on the speed of precipitation. This alloy is completely homogeneous in structure above 525°C., and if made magnetic by precipitation treatment at a lower temperature, will become nonmagnetic again in as little as 4 hr. at 550°C.

The effect of quenching temperature on subsequent precipitation in these dilute alloys is shown more graphically in Figs. 7 and 8. A series of samples was annealed for 1 hr. at 800°C. and one of each alloy was removed and quenched. The remainder were furnace-cooled to 750°C. and held 1 hr., then a second sample of each composition was quenched. This was continued by furnace cooling in steps of 50°C. and annealing for 1 hr. at all temperatures until 300°C. was reached. This rate of cooling does not give equilibrium except at the higher temperatures. Samples from 850° and 900°C. were directly annealed at those temperatures and quenched, but otherwise all samples were treated together and possessed the same grain size. The remanence of the samples was determined in the quenched condition, again after reheating for 241 hr. at 400°C. or 32 hr. at 450°C., dependent on the iron content, and finally after cold-rolling 50 per cent following these

* Time at 800°C., at least within the range of $\frac{1}{4}$ to 2 hr., had no effect on the results. The effect of quenching temperature was approximately the same when the samples were directly annealed as when this temperature was approached by furnace cooling. Furnace cooling was adopted to avoid grain-size changes.

anneals. None of the samples were detectably magnetic in the quenched condition and after reheating the remanence never exceeded 0.2×10^{-3} . The remanence after

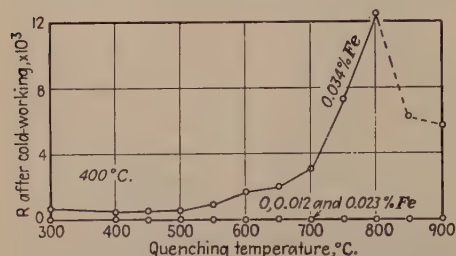


FIG. 7.—EFFECT OF QUENCHING TEMPERATURE ON SUBSEQUENT CHANGE OF REMANENCE ON COLD-ROLLING AFTER REHEATING.

70-30 brass containing iron as indicated. Quenching temperature approached by furnace cooling from 800°C. Quenched samples reheated 241 hr. at 400°C. and cold-rolled 50 per cent reduction. Alloys before cold-rolling were all sensibly nonmagnetic, $R > 0.2 \times 10^{-3}$.

the final cold-rolling is shown in Figs. 7 and 8.

The samples with 0.023 per cent Fe or less failed to precipitate at 400°C., and

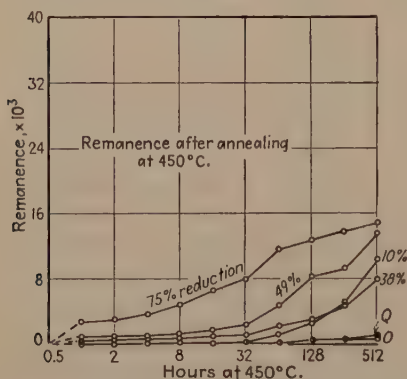


FIG. 9.—EFFECT OF REHEATING AT 450°C. ON REMANENCE OF ALPHA BRASS PREVIOUSLY COLD-ROLLED.

Samples contained 30 per cent Zn, 0.053 per cent Fe and were reheated at 450°C. after quenching from 800°C. (curve Q), quenching from 400°C. after furnace cooling from 800°C. (curve O), and cold-rolling 10, 38, 49 and 75 per cent reduction in latter condition.

that with 0.041 per cent did not change at 450°C. whatever the prior treatment, un-

doubtedly because these amounts of iron were soluble at the temperature concerned. The alloy with 0.034 per cent Fe at 400°C. and those with 0.049 and 0.064 per cent at

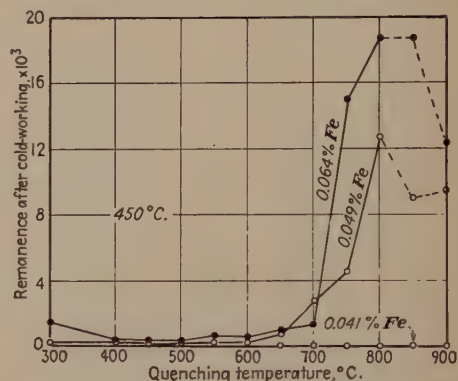


FIG. 8.—EFFECT OF QUENCHING TEMPERATURE ON SUBSEQUENT CHANGE OF REMANENCE ON COLD-ROLLING AFTER REHEATING.

70-30 brass containing iron as indicated. Quenching temperature approached by furnace cooling from 800°C. Quenched samples reheated 32 hr. at 450°C. and cold-rolled 50 per cent reduction. Alloys before cold-rolling were all sensibly nonmagnetic, $R > 0.2 \times 10^{-3}$.

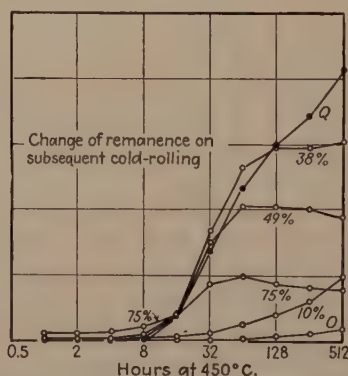


FIG. 10.—CHANGE OF REMANENCE PRODUCED BY COLD-ROLLING THE REHEATED ALLOYS OF FIG. 9; 50 PER CENT REDUCTION OF THICKNESS.

450°C. show a considerable amount of precipitation, detectable after cold-work, if they are quenched from 800°C. and progressively less as lower temperatures are reached.

This effect of quenching temperature is not, as might be supposed, one of quench-

ing strains. Over 30 per cent reduction by cold-rolling must be applied to a sample quenched from a low temperature before the rate of precipitation on subsequent

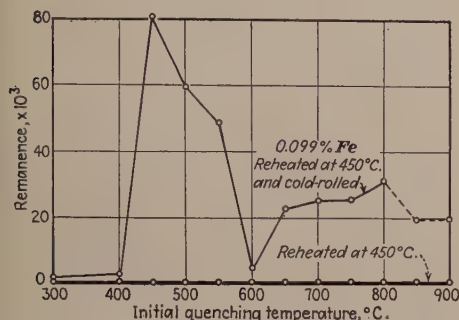


FIG. 11.—EFFECT OF QUENCHING TEMPERATURE ON REMANENCE OF ALPHA BRASS AFTER REHEATING AND COLD-ROLLING.

Brass contained 30 per cent Zn, 0.099 per cent Fe quenched from temperatures indicated after furnace cooling from 800°C. Quenched samples reheated 32 hr. at 450°C. and then cold-rolled, 50 per cent reduction of thickness.

annealing at 450°C. becomes equal to that of a sample quenched from 800°C. In Fig. 9, curve Q represents samples quenched after 1 hr. at 800°C.; curve O, samples annealed at 800°C., furnace-cooled to 400°C. and quenched; curves 10, 38, 49 and 75 represent samples similarly furnace-cooled to 400°C. and quenched, then cold-rolled the percentages indicated by these figures prior to the 450°C. anneal. Fig. 9 shows the remanence after reheating for the times shown, and Fig. 10 the change in remanence as these samples were subsequently rolled 50 per cent and remeasured to show the extent of nonmagnetic precipitation. The sample quenched from 400°C. and given a 38 per cent reduction has approximately the same rate of precipitation as the one quenched from 800°C. and not cold-worked, but this, and even the 10 per cent one, has a much greater amount of directly ferromagnetic precipitate than did the quenched samples. Quenching strains must be of very small magnitude. Still further proof that quenching strains are not involved is given by the

fact that samples quenched from 800°C. in iced calcium chloride solution at minus 18°C., in water at 20° or 99°C., or in oil all had identical properties after reheating.

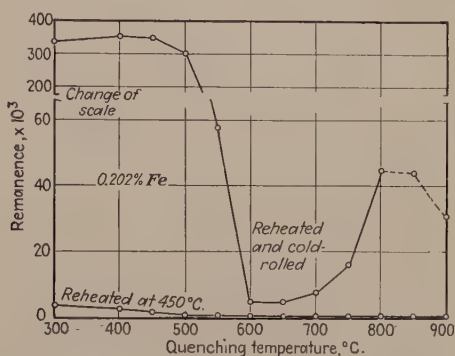


FIG. 12.—EFFECT OF QUENCHING TEMPERATURE ON REMANENCE OF ALPHA BRASS AFTER REHEATING AND COLD-ROLLING.

Brass contained 30 per cent Zn, 0.20 per cent Fe, treated as Fig. 11.

Only after cooling in air or at a slower rate did the remanence after annealing for 135 hr. at 450°C. and cold-rolling drop below that of a normal water quench.

No detectable change of Rockwell hardness occurred during any of these reheating treatments.

BEHAVIOR OF ALLOYS WITH 0.1 PER CENT IRON AND ABOVE

A series of samples of higher iron content were annealed at 800°C., furnace-cooled to various temperatures, quenched, and reheated at 450°C. at the same time as those of Fig. 8. The results are complicated by the fact that precipitation occurred to some extent during furnace cooling and it is hard to differentiate this from that produced at 450°C. Figs. 11, 12 and 13 show results typical of four different iron contents. In Fig. 11 (0.099 per cent Fe) there is a decrease in remanence with quenching temperature above 600°C., just as in the lower iron alloys. This is followed by a marked increase at 550°, and a decrease at 400°C., the latter confirming the behavior of a similar sample in Fig. 5. With 0.202 per

cent Fe (Fig. 12) the drop at the lowest temperatures is absent, and very high remanence is produced by all treatments at 500°C. or below. With higher iron con-

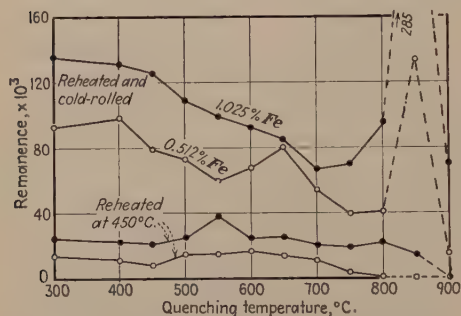


FIG. 13.—EFFECT OF QUENCHING TEMPERATURE ON REMANENCE OF ALPHA BRASS AFTER REHEATING AND COLD-ROLLING.

Brasses contained 30 per cent Zn and 1.025 per cent or 0.512 per cent Fe, treated as Fig. 11.

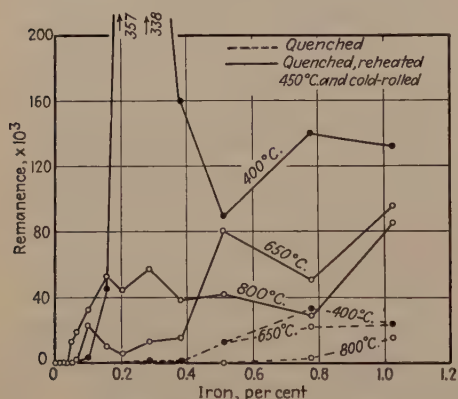


FIG. 14.—EFFECT OF IRON CONTENT ON REMANENCE OF 70-30 BRASS.

Samples quenched from 800°, 650° or 400°C., reheated 32 hr. at 450°C. and cold-rolled 50 per cent reduction.

tents (Fig. 13) there is a significant amount of direct magnetic precipitate, though the change on subsequently annealing and cold-working is less.

The results of all alpha alloys are plotted against their iron content in Fig. 14. The curves in this figure represent the remanence of the alloys as quenched following furnace cooling to 800°, 650° and 400°C., and the remanence of the same samples

after annealing 32 hr. at 450°C. and cold-rolling. The change produced by the 450°C. anneal without cold-rolling was very small. Fig. 15 shows the effect of cold-rolling

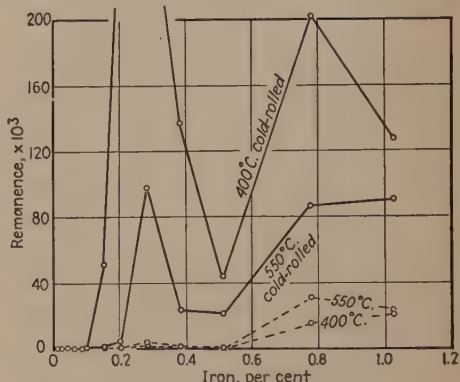


FIG. 15.—EFFECT OF IRON CONTENT ON REMANENCE OF 70-30 BRASS.

Samples furnace-cooled from 800° to 550° or 400°C. and directly cold-rolled 50 per cent reduction without intermediate reheating.

directly after the furnace cooling from 800°C. to 550° and to 400°C. and quench, without the 450°C. treatment. Nonmagnetic precipitation had occurred during cooling to a considerable extent, particularly in the range 0.2 to 0.3 per cent Fe. The fact that there is less of this nonmagnetic form in the alloys of higher iron content is probably a result of the presence of the magnetic precipitate formed at higher temperatures, which provided nuclei for further precipitation. It is evident that a given amount of iron produces much higher remanence when in the form converted by cold-work from the nonmagnetic precipitate than when it exists as free alpha iron. This may be an indication that the transitional form contains a considerable amount of copper and zinc associated with it. Iron in equilibrium with copper at the temperatures concerned contains not over 0.4 per cent of the latter element.

PRECIPITATION OF IRON IN BETA BRASS

Because beta brass is body-centered-cubic in structure, there is little likelihood

of the formation of a nonmagnetic face-centered-cubic transitional precipitate. The precipitated iron is already on a body-centered-cubic lattice and becomes ferro-

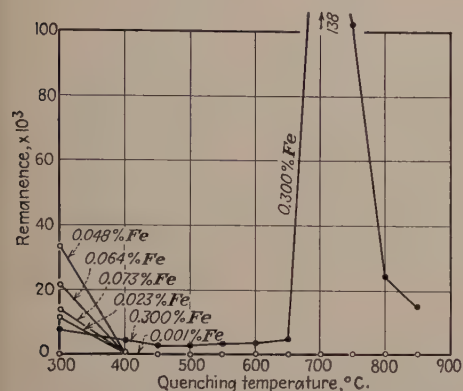


FIG. 16.—EFFECT OF QUENCHING TEMPERATURE ON REMANENCE OF BETA BRASS OF VARIOUS IRON CONTENTS.

Samples quenched from temperatures indicated after furnace cooling from 800°C. Not reheated or cold-worked.

magnetic as soon as its size permits. Subsequent cold-working produces little change. Beta is not, however, without its peculiarities. Quenching a *dilute* alloy of iron in beta brass (47 per cent Zn) from a temperature where the iron is in solution results in a nonmagnetic sample; furnace cooling to a sufficiently low temperature or reheating suitably produces the increase of remanence expected of the iron precipitate formed. This is shown in Fig. 16, wherein alloys with 0.07 per cent Fe or less are seen to be nonmagnetic except on furnace cooling to 300°C., where they all acquire measurable remanence in spite of the short annealing times. On the other hand, alloys with 0.3 per cent Fe or more (Figs. 16, 17) when quenched from a high temperature are very strongly magnetic, even though the iron undoubtedly was in solution at the time of quenching, and the remanence actually decreases as the quenching temperature is lowered to the point at which the iron is thrown out. The results of a series of beta alloys containing iron are

plotted against iron content in Fig. 18. After furnace cooling to 300°C. the samples containing 0.02 to 0.07 per cent Fe are actually more magnetic than those with

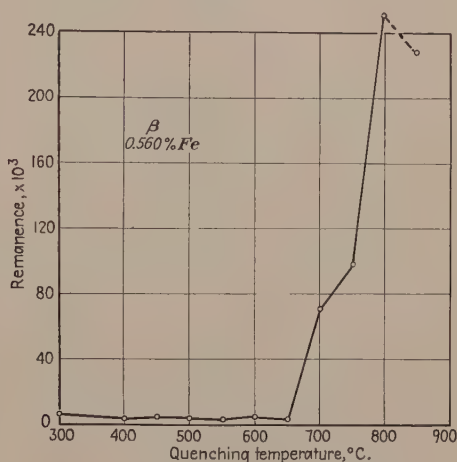


FIG. 17.—EFFECT OF QUENCHING TEMPERATURE ON REMANENCE OF BETA BRASS WITH 0.560 PER CENT IRON. TREATMENT SAME AS FIG. 16.

higher iron. Just as in the alpha alloys, it seems as though some intermediate stage of precipitation is responsible for the highest remanence. The strong ferromagnetism of the samples containing over 0.3 per cent Fe quenched from about 800°C. is surprising. It is unlikely that a true solid solution of the compositions concerned would possess ferromagnetic properties, though their relation to Heusler alloys must not be overlooked. The magnetism is not associated with an ordered structure, for cold-working (by filing) slightly increased the remanence of an alloy with 0.4 per cent Fe quenched from 850°C. and had no effect on one with 0.05 per cent rendered magnetic by furnace cooling to 300°C.

The effect of reheating quenched beta alloys containing iron needs further study. With the strongly magnetic alloys of 0.3 per cent Fe or over quenched from 800°C., 4-hr. anneals produce no change below 400°C., but at 500°C. the remanence drops and the curve thereafter rises as the tem-

perature is increased, in a manner identical with that of the directly quenched alloys of Fig. 17. Low-iron alloys in the nonmagnetic quenched state become strongly magnetic

of iron atoms that must exist as a result of thermal agitation at high temperatures will provide a fair number of potential nuclei¹⁹ or at least of occasional groups of iron

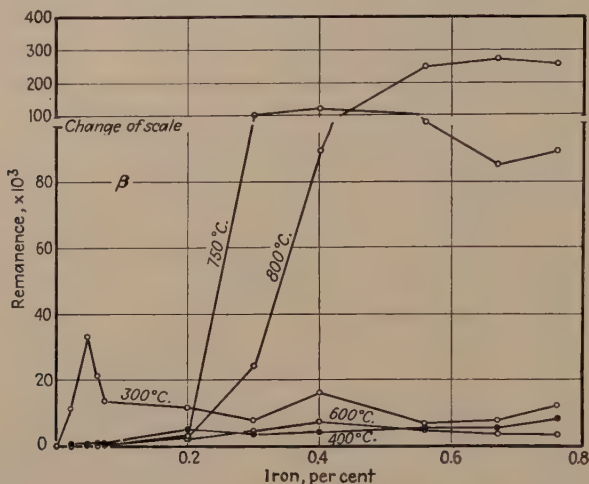


FIG. 18.—EFFECT OF IRON CONTENT ON REMANENCE OF BETA BRASS (47 PER CENT ZINC).

Samples quenched from indicated temperatures after furnace cooling from 800°C. Not reheated or cold-worked.

after a long anneal at 300°C., and more quickly reach a maximum at 400°C., lower than at 300°C. or nonexistent if the iron is below the solubility limit at this temperature. In contrast with the slow precipitation of iron in alpha, the reactions in beta are very rapid.

SPECULATION ON NATURE OF DILUTE SOLID SOLUTIONS

It is difficult to explain the newly observed influence of quenching temperature within the solid solution range on the subsequent rate of precipitation at lower temperatures. It seems that a more stable form of the solid solution exists at low temperatures and it must be assumed that the distribution of the iron atoms is different at different temperatures. The ideal form of a solid solution is probably one in which the solute atoms are as far apart as possible, but thermal agitation destroys this arrangement to a degree increasing with temperature. The random distribution

atoms as relatively close neighbors. No nuclei could form until two or more had migrated by diffusion into adjacent positions, and the time for this to occur would be much less with a statistically disordered solid solution than in the more or less ordered form postulated. The difference between the two forms will become less as the number of solute atoms increases. This varying distribution of solute atoms with temperature is probably characteristic of any dilute solid solution. Its detection will generally be very difficult and the only reason it appears in the present case is that the solute atom has the correct critical solubility relationships and is readily identifiable in minute amounts.

SUMMARY

Iron in excess of 0.03 per cent can be precipitated from 70-30 brass by suitable low-temperature annealing. Precipitation is slow and occurs chiefly in a transitional

nonmagnetic form that is converted to a ferromagnetic structure on cold-working. The rate of precipitation in dilute alloys is greatly dependent upon prior quenching temperature. Quenching from about 800°C. produces the most rapid subsequent precipitation at 400° to 500°C. Air cooling from 800°C. or quenching from lower temperatures causes progressively slower precipitation even though the alloys are definitely homogeneous when quenched. The effect is not due to quenching strains and is assumed to be associated with the location of the iron atoms in the parent lattice.

Beta brass containing 0.3 per cent Fe or above is ferromagnetic when quenched from the solid solution range, and actually becomes less magnetic as iron precipitates during annealing at lower temperatures. Beta brass with less than 0.2 per cent Fe is nonmagnetic when quenched from the solid solution range but readily precipitates iron at low temperatures in a directly magnetic form that is not affected by cold-working. These statements are based upon remanence measurements in a simple apparatus.

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DISCUSSION

(S. Skowronski presiding)

L. A. CARAPPELLA,* Washington, D. C.—Among other valuable contributions contained in this paper, Dr. Smith has shown, in detail, that the cold-working of a number of brasses after a precipitation-treatment rendered them ferromagnetic. A proposed explanation for this behavior is that the precipitate (iron) occurs initially in a transitional nonmagnetic form which, upon cold-rolling, is converted to a ferromagnetic structure.

If this structure represents the stable alpha (body-centered-cubic) modification of iron, a strain-anneal treatment after cold-rolling should not destroy its ferromagnetic nature. Some decrease, however, is to be expected, since the remanence measured after cold-rolling is, principally, the sum of two factors; the amount of converted (ferromagnetic) iron present, and the degree to which its lattice is distorted. Plastic deformation alone has been shown to increase the residual induction of iron; hence, by strain annealing, its effect can be eliminated. As a matter of interest, has the author given any consideration to this factor?

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Moreover, it has been pointed out by Dr. Smith that a higher remanence is found in iron converted by cold-rolling from the transitional nonmagnetic form than in an equal amount of free alpha iron. He attributes the difference to the presence of a considerable amount of copper and zinc in the transitional form. In the light of the above discussion, might not the explanation be the presence of plastic distortion alone, rather than a composition effect?

A. R. KAUFMANN,* Cambridge, Mass.—One of the most interesting results of Dr. Smith's work is the demonstration that iron, when precipitating from beta brass, comes out directly in the magnetic form, whereas the precipitate from alpha brass is in the nonmagnetic form. This behavior lends some support to the idea that the face-centered lattice of copper or alpha brass exerts a constraining influence on the precipitating iron atoms and prevents them from forming their equilibrium body-centered lattice.

As a matter of interest, I might point out that when iron precipitates from gold there is no evidence of a transition structure, and the system gold-iron is very similar to copper-iron, both from the metallurgical and physical standpoint. This would indicate that other factors in addition to the crystal structure of the solvent phase must be considered.

With regard to some of Dr. Smith's other conclusions, I think he should be even more cautious than he has been in interpreting the observations on remanence. As he has already pointed out, remanence depends on many very complex factors, such as the composition of the particles, their shape and also the absolute size of the precipitate, and therefore there is no direct relationship between the measured remanence and the amount of precipitated iron. This is well brought out by Dr. Smith's data in Figs. 2 and 14. Therefore, since remanence is not at all a reliable indication of the magnitude of the precipitate, I think it is quite dangerous to draw conclusions as to the rate of precipitation as Dr. Smith has done.

The observed results might be accounted for in quite a different way. I am referring now to the apparent effect of the quenching temperature above the solubility limit on the rate of

precipitation. One might assume, for instance, that what has happened is that the size of the precipitated particles during aging is influenced by the quenching temperature and not necessarily the rate of precipitation. If the precipitate came out, let us say, as very fine particles in the alloy quenched from high temperatures and as coarser particles in alloys quenched from lower temperatures, a marked difference in the remanence just of the sort observed would be expected. I believe also that this behavior would be somewhat more in accord with the theory of just what a solid solution is.

Dr. Smith assumes that in a solid solution of this type the dissolved atoms are trying to get as far apart as possible, whereas actually the reverse is true. Where there is a solubility limit, the tendency is for the atoms of the two kinds to separate into the pure metals, and this tendency is counteracted by thermal agitation, which tries to mix them. The solubility limit at any temperature is determined by a sort of balancing of these two forces. In the solid solution range the nearer the solubility limit is approached, the greater the tendency would be for the dissolved atoms to come together in the form of nuclei, and the higher the temperature above the solubility limit, the more randomly they would be distributed. Hence it is quite conceivable that a specimen quenched from just above the solubility limit would contain nuclei that would facilitate subsequent precipitation in the form of large particles, whereas an alloy quenched from higher temperatures would be forced to precipitate in the form of very small particles, which would have a higher remanence than the coarse precipitate.

With regard to the idea that beta brass containing 0.3 per cent or more of iron in solid solution is ferromagnetic, I would like to point out that the magnitude of the remanence reported by Dr. Smith could easily be accounted for by a small fraction of the iron that is known to be present in the alloy, if that iron had not been retained in solid solution. Therefore, a much more reasonable explanation of the observations would be simply that for some reason or other quenching has not retained all the iron in solid solution. This is further substantiated by the fact that if the whole solid solution had become ferromagnetic, the magnitude of the observed remanence would unquestionably be much greater.

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S. E. MADDIGAN,* Waterbury, Conn.—Under ordinary conditions one would expect the body-centered form of iron to be precipitated below a temperature of 860°C. Since

point, both phases are equally stable and the transformation from one phase to the other is reversible. For any other condition the transformation is irreversible, and can occur only

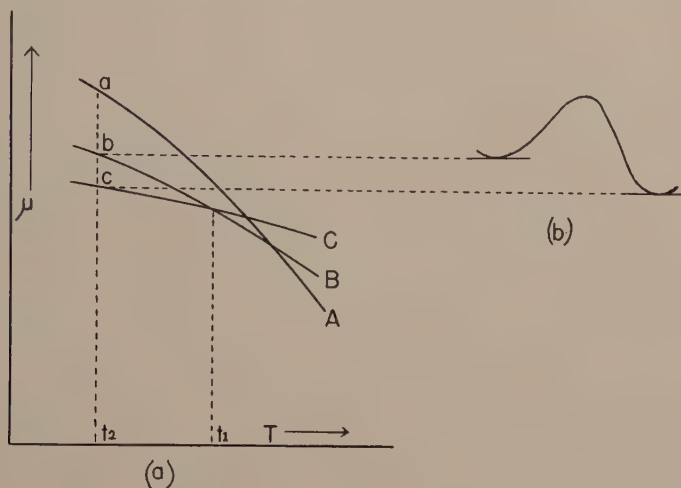


FIG. 19.

Dr. Smith's concept concerning precipitation of the normally unstable face-centered-cubic iron is a radically new thought in physical metallurgy, I would like to draw attention to a considerable mass of supporting data existing in nonmetallurgical literature.

According to Tammann,²¹ the thermodynamic potential $\mu = U - TS - PV$ is a measure of the stability of a phase,

where U = internal energy,

T = temperature,

S = entropy,

P = pressure,

V = volume.

All processes in nature tend to proceed until the entropy S reaches a maximum or until the thermodynamic potential μ reaches a minimum. Plotting values of the thermodynamic potential in a μPT space, one finds that for each phase a surface exists along which the phase is stable. For simplicity, the pressure P can usually be taken as constant, in which case the phase is stable along some curve such as B in Fig. 19 plotted on μ - T coordinates. A second phase is stable along some curve C , which intersects B at the transition temperature " t_1 ." At this

in the direction of decreasing " μ " as, for instance, from b to c at t_2 . This is equally true whether the phase changes considered are for example liquid-solid, gas-solid, solution-solid, or merely between two solid phases of a polymorphous substance.

From the above, one might expect that a substance could exist only in the condition of maximum stability; i.e., in the phase with minimum thermodynamic potential. That such is not true is evident, since several polymorphous materials are found in natural minerals in more than one phase, though one phase may have a definitely lower thermodynamic potential than the other under the conditions of existence; e.g., graphite and diamond. This is because except at the transition point the transformation velocity may be extremely small in some cases. In the language of reaction kinetics, it may be stated that between the energy levels of the two phases there exists an energy peak over which the unstable phase must travel in order to reach the lower energy level of the stable phase (Fig. 19b). In the absence of external energy sources this activation energy to cross the peak is usually supplied by thermal fluctuation. Thus, the transformation velocity decreases

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²¹ *Ann. phys.* (1913) 40, 297.

as the temperature is lowered below the transition point. According to Shoji,²² the velocity varies inversely as the distance below the transition temperature.

In a transition from a high energy level when two or more possible lower energy levels exist, the transition frequently proceeds by stages. Instead of transforming immediately to the phase of lowest thermodynamic potential, the phase of intermediate value may be produced, and then later a further transformation to the phase of lowest value may occur (Ostwald Rule); e.g., in Fig. 19a a vapor at temperature t_2 with $\mu = a$ may transform first to the liquid with $\mu = b$, and later a further transformation may occur from the liquid at b to the solid at c , although from purely thermodynamic reasoning since t_2 is well below the melting point at t_1 the transition would be expected to go directly from a to c . Classical examples of such a process are the condensation of sulphur and of phosphorus vapors, which condense first to a liquid even when well below the melting point.

Stranski has examined a similar case for a polymorphous material.²³ HgI_2 has two solid forms, a red modification stable below 126°C ., and a yellow form stable above that temperature. In deposition from the vapor below the transition temperature, Stranski found, in fact, that the high-temperature form was produced in major quantities, though some of the low-temperature red form was also deposited. The relative abundance of these forms depended on the temperature, with a probability relationship agreeing with Stranski's mathematical theory of nucleation and growth.

Several experimenters have produced data indicating that the crystal form of surrounding media will affect the course of a phase change. Stranski has shown that above 50.7°C . sodium bromide precipitates as a mixture of NaBr and $\text{NaBr} \cdot 2\text{H}_2\text{O}$. If precipitated on a surface of PbS (lattice almost identical with NaBr) the mixture contains greater percentages of the anhydrous form than under normal conditions.

Somewhat analogous to the precipitation of iron from solid solution in brass is the formation of mixed crystals from aqueous solutions. Bunn²⁴ and other workers have shown that in

precipitation of certain salt crystals from solution the crystal habit of growth may be entirely changed by small additions of a second salt, which is coprecipitated as a mixed crystal. Furthermore, definite orientation relations exist when one of these salts is precipitated as an overgrowth upon a crystal of the other. It has further been found that certain insoluble salts can precipitate some others as overgrowths from *unsaturated* solutions, provided the two salts have similar lattices with atom separations differing by less than about 10 per cent.²⁵

All these phenomena indicate that proper structural relationships between a given substance and the surrounding media can seriously influence the stability conditions during a phase change.

More closely analogous to the case being considered are data from electron diffraction investigations. By depositing in thin films upon basis materials with suitable crystal structures, hexagonal forms of both nickel and aluminum have been discovered, though these metals have been known previously only in the cubic form.

The present writer has investigated the effect of the basis crystal structure upon polymorphous materials deposited from the vapor phase.²⁶ ZnS has a cubic form stable at room temperature, and a hexagonal form stable only at extremely high temperatures. When deposited from the vapor on to glass below the transition temperature, a mixture of the phases was found just as Stranski found for HgI_2 . However, when deposited on a basis substance with a structure similar to that of cubic ZnS , the film contains mainly cubic ZnS ; when the basis had a structure similar to that of hexagonal ZnS the deposited film contained mainly the hexagonal form. Once the deposit was formed it could be removed from the basis without disturbing the relative proportions in the mixture, owing to the activation energy necessary for a transition. As in Goldschmidt's work, the atom separation in the basis material had to be within about 15 per cent of that for the given ZnS phase in order to be effective.

In the present case copper and gamma iron belong to the same space group o_h ²⁵ and their lattice constants differ by less than 10 per cent.

²² H. Shoji: *Ztsch. Kryst.* (1931) **77**, 397.

²³ Stranski and Totomanow: *Ztsch. phys. Chem.* (1933) **A-163**, 399.

²⁴ C. W. Bunn: *Proc. Roy. Soc.* (1933) **141**, 567.

²⁵ Goldschmidt: *Trans. Faraday Soc.* (1929) **25**, 268.

²⁶ Lark-Horovitz and Maddigan: *Phys. Rev.* (1933) **44**, 320; also Ph.D. Thesis, Purdue University, 1936.

In precipitating from solid solution in a disperse form crystallites of iron would be in even more intimate contact with the brass lattice than in either the ZnS experiments or in the electron diffraction experiments with nickel and aluminum. One would then expect iron to precipitate from alpha brass mainly in the gamma form, although small amounts of alpha iron might also appear following the probability expression of Stranski. Once formed, the gamma phase would continue to exist until sufficient activation energy was supplied to cause a transition to the stable phase. From the structural standpoint, the face-centered iron can be transformed into the body-centered form by a contraction on one crystallographic axis and an expansion on the other two axes. Thus, working of the brass containing precipitated gamma iron would be expected to supply the activation energy for a transition to the stable form. By breaking up the brass crystals into small slightly disregistered blocks, working would also tend to reduce the control of the alpha brass on the precipitated iron and make the transition easier.

By a similar effect, severe working prior to the precipitation anneal would reduce the control of the alpha-brass lattice on the precipitate at regions of disregistry. Thus, a considerable amount of the precipitate should be alpha iron.

F. W. CONSTANT,* Durham, N. C.—The experiments and results described in this paper are of much interest to me. With my co-workers at Duke University I have performed a number of experiments on the ferromagnetic properties of commercial copper wire and brass rods, using the same simple method of measuring the magnetic remanence. Some of our results are contained in references 17 and 18 of Dr. Smith's paper, but subsequent work awaits publication, and I should like to mention a few points from it that may pertain to this paper.

Using ordinary yellow brass (33 per cent Zn), in the form of small rods, the remanence was measured before and after heating for 8 hr. at various temperatures from 100°C. to 800°C. and quenching in water. When quenched from 400°C. the remanence increased from two to five times its original value, depending on the

sample used. But for the higher temperatures the remanence fell off rapidly and it disappeared after heating and quenching at 780°C. In the last case reheating at 450° restored some of the magnetism, and presumably cold-work would serve the same purpose. As the initial remanence of this brass represented a magnetic moment per cubic centimeter of around 10^{-2} the iron content was probably under 0.1 per cent. Hysteresis loops were run on samples before and after heat-treatment. These showed that the increase in remanence at 400°C. was largely due to increase in magnetic hardness. The disappearance at high temperatures is attributed to solution of the iron in the alpha brass.

Samples of zinc were tested in a similar way. In no case was any remanence observed.

Turning to copper, samples of No. 12 D.C.C. wire were used, after proper surface cleaning. Heat-treatments in a hydrogen atmosphere revealed results similar to those for brass, only the peak remanence occurred after heating to 550°C. and remanence disappeared after heating to 900°C. The original remanence was about one twentieth that for the brass and the peak remanence five to six times the original.

When a nitrogen atmosphere was substituted for hydrogen, surprising differences were noted. First the peak at 550°C. disappeared, but a new one appeared at 900°C. and remanence disappeared only after heating to 1040°C. Careful investigation revealed that these new effects were due to oxygen present in the tank nitrogen. Further, it was found that presence of oxygen assisted a return of remanence in specimens earlier rendered nonmagnetic in hydrogen at 900°C. Evidently the oxygen can diffuse into the copper only above about 850°C. and when it does so it may oxidize the iron impurity into a magnetically "hard" form. Hydrogen at high temperatures would reduce such oxides to pure iron, which could then dissolve in the copper lattice. It is clear, at least, that in such experiments the atmosphere used plays an important part.

C. S. SMITH (author's reply).—The change in ferromagnetism that results from cold-working an alloy with the nonmagnetic iron precipitate is so great that it seemed unlikely that it could be due entirely or even largely to strain in alpha-iron particles. Nevertheless some addi-

* Duke University.

tional measurements were carried out to investigate Dr. Carapella's hypothesis, the results being shown in Fig. 20. This relates to 70-30 brass containing 0.10 per cent iron, the

supposedly because of progressive solution of the iron. Cold-working the reheated samples (curve C_w) has an effect that may be due to strain in the magnetic precipitate to the con-

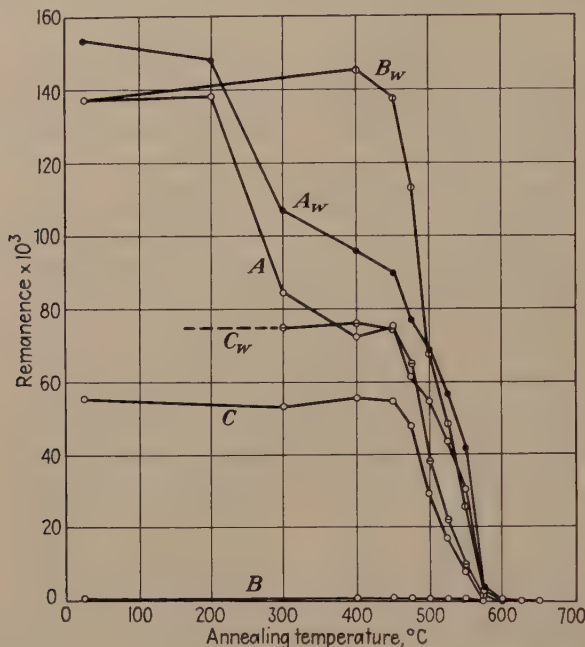


FIG. 20.—REMANENCE OF 70-30 BRASS CONTAINING 0.10 PER CENT IRON AFTER VARIOUS TREATMENTS.

Curve A Quenched from 800°C., annealed 140 hr. at 450°C. and cold-rolled 50 per cent reduction before annealing for 4 hr. at temperatures plotted.

A_w As A, then further cold-rolled 50 per cent reduction.

B Annealed 140 hr. at 450°C., reannealed 4 hr. at temperatures plotted.

B_w As B, subsequently cold-rolled 50 per cent reduction.

C Rolled 75 per cent reduction, annealed 140 hr. at 450°C., then reannealed 4 hr. at temperatures plotted.

C_w As C, then cold-rolled 50 per cent reduction.

same alloy as that shown in Figs. 2 and 5. The effect of heating for 4 hr. at temperatures between 200° and 650°C. was studied on samples A quenched from 800°C., reheated 140 hr. at 450°C., and cold-worked 50 per cent reduction to render them strongly magnetic; B treated as A, but without the final cold-working, i.e., containing the precipitate in nonmagnetic form; and C reheated 140 hr. at 450°C. after cold-rolling 75 per cent reduction following an 800°C. quench, thus giving an unstrained magnetic precipitate. As can be seen in curve C, Fig. 20, heating the latter has no effect until a temperature of over 450°C. is reached, when the remanence decreases rapidly,

version of additional previously nonmagnetic precipitate, or possibly to nothing more than the effect of the more elongated shape of the particles. The alloy when converted from the nonmagnetic to the magnetic form by cold-work (curve A) loses nearly a half of its remanence on annealing at 300° to 450°C., an effect that is probably a result of the loss of strain proposed by Dr. Carapella. The lost remanence is by no means completely restored by further working (curve A_w), indicating that strain comes from the transformation as well as from external causes. The samples containing the nonmagnetic precipitate, when reheated before cold-working, show (curve B_w) virtually

no change until the reheating temperature exceeds the original temperature of precipitation ($450^{\circ}\text{C}.$), when the remanence commences to decrease as the iron goes back into solution. 0.10 per cent iron is completely in solution even after 4-hr. anneals between 575° and $600^{\circ}\text{C}.$ An alloy containing 0.05 per cent iron similarly became nonmagnetic just above $525^{\circ}\text{C}.$

Dr. Kauffmann's additional caution against misinterpretation of remanence measurements is very welcome. I readily agree that remanence change is not a measure of amount of precipitation but rather is a complex function of shape, size, distribution and composition of the ferruginous particles. On the other hand, no other method of studying this problem permits so rapid a survey of a multitude of specimens and treatments. Had it been necessary to build an apparatus and to devote the time necessary for the determination of susceptibility over a wide range of field strengths—measurements of susceptibility at a single field strength or in weak fields are apt to be as misleading as remanence—the fact that an interesting change of some kind occurred in the solid solutions under discussion might have remained unobserved.

The behavior of the gold-iron system, referred to by Dr. Kauffmann, is not in disagreement with my theory. The match between the face-centered-cubic lattices of copper or alpha brass and gamma iron is within 3 per cent ($A_0 = 3.608$ for copper, 3.673 for 70-30 brass, 3.562 for gamma iron, by extrapolation). Gold

however ($A_0 = 4.070$) is 14 per cent larger than iron and registry is so poor that the mother gold lattice would provide very little constraint to the embryo.

My views on the distribution of solute atoms in solid solution remain unchanged by Dr. Kauffmann's remarks thereon. The condition he describes of local clustering of atoms seems to me to characterize a supersaturated solid solution in an early stage of precipitation and not to represent a stable unsupersaturated solution.

The theoretical justification for the proposed precipitation mechanism and the confirmatory examples from other systems quoted by Dr. Maddigan are very welcome. Metallurgists in general would do well to heed his polite and erudite reminder that metals follow the same laws as do other substances. The keys to many metallurgical perplexities are to be found in analogous nonmetallic systems. It is to be hoped that now that he has forsaken the quiet and lofty dwellings of the physicist for the bustle of the lowly metalworks Dr. Maddigan will continue to have time to survey the entire literature of physics and chemistry!

Anticipation of difficulties with the oxidation of iron in copper was partly responsible for the choice of brass instead of copper for the work described in the paper. It is good, therefore, to have Dr. Constant's experimental results showing conclusively that oxygen is an important factor in determining the condition of iron in copper and hence its magnetic properties after various heat-treatments.

Micrographic Observations of Slip Lines in Alpha Brass

By R. G. TREUTING,* STUDENT ASSOCIATE, AND R. M. BRICK,† MEMBER A.I.M.E.

(Philadelphia Meeting, October 1941)

DESPITE the basic importance of slip in the plastic deformation of metals, and the considerable experimental investigation, thought, and speculation that have been devoted to the fundamental nature of these processes, surprisingly few data have been reported regarding the microscopic appear-

etching produced a surface free of both scratches and flow.

The specimen was strained in tension until slip markings first became visible on the polished surface (Figs. 1 and 2). Restressing the crystal caused additional markings to appear at an initially lower



FIG. 1.—ORIGINAL CRYSTAL, 0.006 SHEAR. $\times 4$.

ance and distribution of slip lines,‡ the external manifestation of the slip process. Photographs hitherto reproduced in the literature are in general at low or unspecified magnifications with no correlation to the prior shear.

A single-crystal cylindrical tensile specimen of alpha brass about $\frac{1}{2}$ in. in diameter, one of many previously prepared by H. L. Burghoff,¹ was available for study. A plane about $\frac{3}{16}$ in. wide, parallel to the specimen axis and normal to the plane containing the slip direction and the specimen axis, was ground and metallographically polished along the entire 5-in. gauge length. Heavy

stress than previously was required. Stretching the specimen to produce a dense concentration of slip lines caused such variations in level in the polished surface (normal to the slip direction) that microscopic study at higher magnifications became impossible.

After annealing 15 hr. at 850°C., the specimen recrystallized to form two grains with a boundary approximately normal to the specimen axis and about midway along its length. Each was X-rayed, and two planes were again polished along the length of the specimen, in this case each parallel to the slip direction in one of the two crystals. A light longitudinal scratch parallel to the specimen axis was drawn down the center of each plane. A Huggenberger extensometer was attached to the crystal A, whose slip plane would have the higher resolved shear stress of the two, and the specimen was again strained in tension.

Manuscript received at the office of the Institute March 18, 1941. Issued as T.P. 1356 in METALS TECHNOLOGY, August 1941.

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‡ The more familiar term "slip bands" is misleading in that it suggests markings of appreciable width.

¹ References are at the end of the paper.

The crystal began to show slight plastic behavior just before it began to flow with no increase in load at its "yield point." Slip lines did not become visible to the eye

tively. Up to this time crystal *B* showed no evidence of slip.

The extensometer was transferred to crystal *B*, and the specimen was strained



FIG. 2.—ORIGINAL CRYSTAL, 0.006 SHEAR. $\times 2000$.



FIG. 3.—CRYSTAL *A*, 0.056 SHEAR. $\times 4$.

until after this flow had begun. A marking on crystal *A* was photographed at its point of intersection with the longitudinal scratch (Fig. 4), on the plane parallel to its slip direction. The specimen was successively stretched five times more to the yield point of crystal *A*, each time with the appearance of new slip lines. Figs. 5 and 6 were photographed at the same spot as Fig. 4, after the second and sixth extensions, respec-

a seventh time, to the yield point of this crystal. A few slip lines appeared on its surface while those on crystal *A* became very dense (Fig. 3). The elongation of the latter was measured in a 2-in. gauge length, which included the densest concentration of lines. Figs. 7 and 8 were taken at the same point on crystal *A* as Figs. 4 to 6, at different magnifications. The difficulty in focusing the entire field at high magnifi-



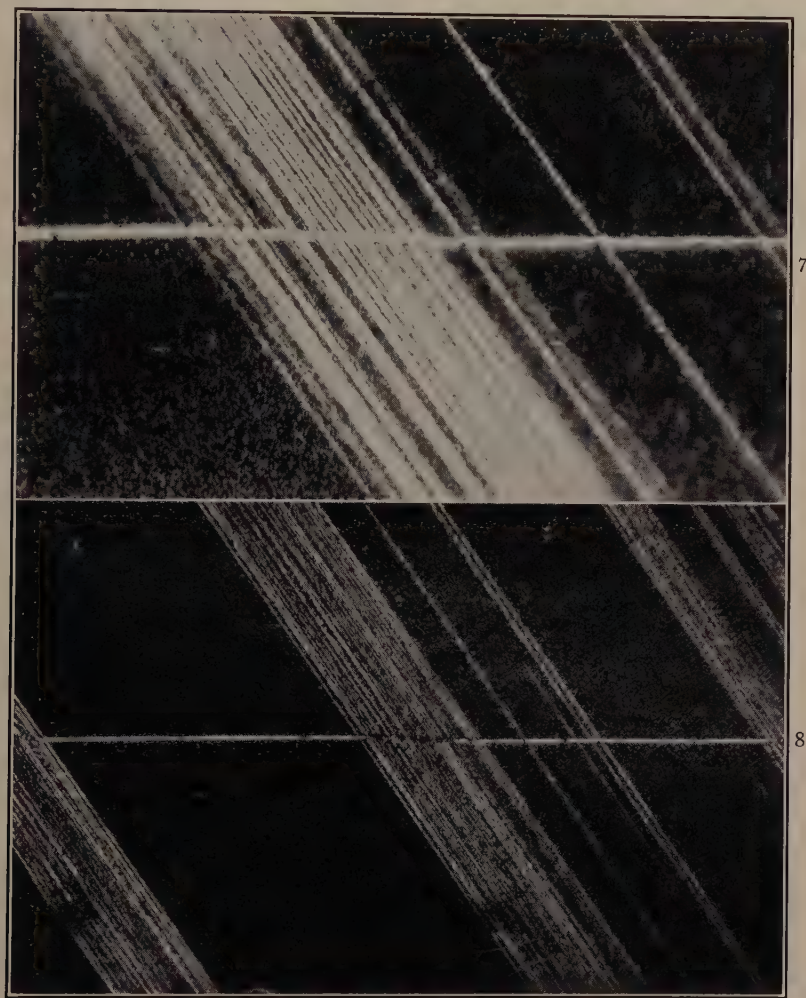
FIGS. 4-6.—CRYSTAL A, $\times 800$.
Fig. 4, 0.002 shear; Fig. 5, 0.004 shear; Fig. 6, 0.015 shear.

cation with increasing amount of strain is due to the rotation accompanying slip.

Stress-strain curves were drawn from the extensometer readings of the first six extensions of crystal *A* in the hope that a definite

progressive drop in the yield point in three successive tensile stressings to the appearance of slip lines on a similar crystal.

The essential stress and strain data regarding the crystals are given in Table 1.



FIGS. 7 AND 8.—CRYSTAL *A*, 0.056 SHEAR.
Fig. 7, $\times 500$; Fig. 8, $\times 200$.

relation between yield point and previous deformation might be obtained. The evidence was irregular; the correlation expected was not observed, and the curves have not been reproduced. However, other tests (by D. L. Martin) have shown a

The shear a and resolved shear stress S on the active slip plane were calculated from the formulas given by Schmid and Boas.²

The resolved shear stresses at which slip lines first became visible are consistent with, although in all cases lower than, the

values reported by Burghoff.¹ This may be due to the subjective nature of the observation and the greater ease with which the markings may be detected on a polished surface.

The orientations of crystals *A* and *B* both differed from that of the original

TABLE I.—*Stress and Shear Data*

Crystal	Figure	Magnification, Diameters	Gross Elongation, Per Cent	Shear, α	Resolved Shear ^a Stress S , Grams per Sq. Mm.
Original....	1	4	0.3	0.006	
Original....	2	2,000	0.3	0.006	1,275
Original....			3.75	0.074	1,245
A.....	4	800	0.089	0.002	1,235
A.....	5	800	0.176	0.004	
A.....	6	800	0.693	0.015	
A.....	7	500	2.64	0.056	
A.....	8	200	2.64	0.056	
A.....	3	4	2.64	0.056	
B.....					1,095

^a Resolved shear stress at which new or additional slip lines first became apparent.

crystal.* That recrystallization took place at all after a shear of but 0.074 would be surprising did not this figure represent an average over a 5-in. gauge length. A given local value may have been much greater. The recrystallized grains still showed a mosaic structure (multiple Laue spots) although to a less degree than the original. (The same observation has been made for other recrystallized grains from cast alpha brass crystals.) A Laue photogram taken on the original crystal at a section of dense slip markings after the 3.75 per cent elongation showed no appreciable change of the pattern from that of the undistorted crystal, in agreement with Wood's observation.³

In each of the three crystals, slip lines on their initial appearance were by no means uniformly spaced. After larger deformations, however, the distribution be-

comes more, though not entirely, equalized (Fig. 3).

The first visible slip line, appearing as a single line to the naked eye, is at high magnification resolvable into a multitude of finer slip markings. The slight non-parallelism and occasional discontinuities of the structure observable in Fig. 3 may well be real, although it is not impossible that it may be an effect from high magnification of a slightly imperfect surface.

Figs. 4 to 8 demonstrate the effect of continued strain (or shear) on the appearance of the lines; at a single macroline, the number of parallel micromarkings increases. Apparently slip preferentially occurs in the immediate vicinity of a prior movement. The lines do not show a well-defined minimum spacing with all others located at a simple numerical multiple of this minimum value. However, the minimum distance between *resolved* lines (Fig. 2) is approximately 2000 atom diameters. The displacement of the scratch in Fig. 4 suggests a shear on the order of 700 atom diameters per active micrographically resolved slip plane, and the evidence is that once this shear has occurred further slip occurs at the next block spacing (about 2000 atoms away). This proposition should be qualified by the observation that the markings are not sharply resolved and may in reality represent an integrated movement over a relatively large number of atomically adjacent planes.

The offset of the originally straight scratch line is evidence of the shear taking place. Measurements of the amount of shear from the photographs are too gross for strict comparison with the theoretically calculated values. The two are not inconsistent, however.

Mathewson has recently proposed a theory of plastic deformation,⁴ one consequence of which is a retained elastic shear strain in the planes immediately adjacent to one on which slip has previously oc-

* An apparent twin relationship between the original and new crystals seems to be invalidated by an irrational axial rotation. Additional single and polycrystal specimens are being studied to determine whether this correlation can be confirmed or should be discarded.

curred, resulting in a slightly reduced resolved shear stress requisite for further slip on the next block slip plane. The micrographic observations on the present brass crystals are in accord with the proposed theory, although they are not necessarily inconsistent with other theories; e.g., dislocations.

Burghoff and Mathewson in a recent paper⁵ have correlated observed creep rates of alpha-brass single crystals with the rate of appearance of visible slip lines. In view of the evidence presented here that a visible slip line may be resolved into finer parallel ones of a number indeterminate save at high magnifications, and that slip may proceed in the region of a marking without any change being detectable by macroscopic methods, the value of such a correlation save in a qualitative sense may be open to question. This need not invalidate these authors' proposition that "slip first occurs on a few planes and then takes place on additional planes . . .," but might rather substantiate it.

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DISCUSSION

(L. S. Fletcher presiding)

H. L. BURGHOFF,* Waterbury, Conn.—The authors have shown excellent photomicrographs of slip lines on their specimens. With regard to the multiple nature of slip markings, it has been generally appreciated by those who have worked with single crystals that the slip markings observed in deformed specimens can be resolved into a number of finer markings with the aid of a microscope.

The number of affected planes that give visible evidence of deformation in any one marking or line is still a matter of speculation,

as Mr. Treuting stated in his presentation, for it surely cannot be that the action on only one atomic plane produces what we call a slip line at any magnification yet at our disposal.

The authors' testing procedure involved straining, release of stress, microscopic examination of strain, restraining, and so on. One may naturally wonder if the appearance or incidence of the successively formed slip lines in this stepwise straining would follow the sequence of events that would take place if the specimen had been strained to the same total extent in one operation. Although it is presumed that the present work was carried out within a reasonably short time, it is conceivable that recovery effects, which can occur in such crystals at ordinary temperatures after a period of time, might somewhat alter the progression of slip.

The initiation of deformation in such crystals is an interesting and not always consistent effect. Sometimes, as in the present work, the first plastic deformation is evidenced by the appearance of markings distributed at random through the test section, with the spacing becoming more equalized as the deformation and the number of markings increase. In other cases, however, the deformation may start at a point on the specimen and then progress steadily from that region throughout the remainder of the test section.

P. W. BAKARIAN,* Midland, Mich.—I followed the progress of this work, and can appreciate the very careful technique that was required to obtain the fine photomicrographs.

Investigations along this line are of first-order importance for obtaining substantiating or nullifying data on the various theories of plastic deformation formulated by such men as Prof. C. H. Mathewson and G. I. Taylor. Therefore, any method that could magnify the happenings on the surface of polished and deformed metal 8 or 10 times more than that observed in the present paper would be even more enlightening. Within the last few months Zworykin and Ramberg,⁶ of the R.C.A. Laboratories, have disclosed a method of applying the electron microscope to observations on metal surfaces at very high magnifications. This

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⁶ V. K. Zworykin and E. G. Ramberg: *Jnl. of Applied Physics* (1941) **12**, 692.

method, which uses a specialized technique, would be directly applicable to investigations of the present type, where very high magnifications are desirable to see just what happens at the slip boundaries, especially for the very small amounts of deformation. In its disclosed form the Zworykin and Ramberg technique was applied to observations on the structure of pearlite at magnifications of 18,000 to 20,000 diameters. The technique involves the evaporation of silver in a vacuum onto the surface to be studied. This film is then stripped mechanically from the surface, yielding a negative metal replica of the surface. From this negative a positive collodion film is made, which is used as the object in the electron microscope.

The application of this high-magnification technique to the study of the slip markings formed in metal crystals during the initial stages of deformation, where, as shown in this paper, they appear in highly localized positions, should indeed be fruitful.

T. T. READ,* New York, N. Y.—The structures shown as the result of tensile stresses are so reminiscent of those observable in rocks, and there attributed, usually, to compression, that the reader is reminded that the study of metal structures under the microscope grew out of the earlier use of the microscope, by Sorby, Zirkel, and others, to study structures in rocks and minerals. Later F. D. Adams, F. Kick, von Karman, and others attempted experimental development of these structures, with a view to better understanding of their cause. In recent years workers in the metal field have carried their studies of structures produced by stresses so much farther than the geologists (with so much more difficult materials to work with) have been able to do that it may be of interest to note that a recent work⁷ on structural petrology turns to the metal field for illustration of structures, and to principles deduced from metals for the interpretation of rock structures. One might say that the geologists cast their bread on the waters and it has returned to them with butter on it. It also illustrates the wisdom of the decision, in the early days of our Institute, to hold together in a single group all those interested in mineral materials, even though their detailed interests

seem widely divergent, on the ground that work in one field will, from time to time, throw important light on problems in some other field.

R. G. TREUTING AND R. M. BRICK (authors' reply).—Dr. Burghoff has raised a question regarding the possibility that recovery effects, between successive stressings of the crystals, may alter the progression of slip. The period of time elapsing between successive stressings was, in general, only that necessary to remove the crystal, rephotograph it, and replace it in the tension machine. At most, one day passed between one strain increment and the next. It would be difficult to estimate the degree of recovery effected during this time at room temperature in a very slightly strained crystal, but undoubtedly it would be small. We were interested primarily in the progression of slip although observations of many crystals have not disclosed any differences between the slip lines formed by successive slight strains and those resulting from one uninterrupted strain of equal total deformation. Although the initial distribution of slip markings may be non-uniform, in all cases, there appeared to be a tendency toward equalization of distribution over the total gauge length with increasing strain and slip. We suspect any initial irregularities to be due to inhomogeneity of stressing or inhomogeneity of the crystal structure, or both.

The new electron microscope technique giving high resolution of metallic surfaces, referred to by Dr. Bakarian, may well prove a valuable tool to the metallurgist, subject always to the condition that the technique employed produces no alteration of the surface under examination.

We are most interested in Professor Read's informative comments and are pleased that work in this field should prove of any service to the geologist or petrographer. Ignorance precludes our making any direct contribution or suggestion ourselves.

Since the presentation of this paper it has come to our attention that Andrade⁸ has published a photograph of slip lines in lead at 800 diameters magnification. This shows incomplete lines running from top to bottom, which terminate close to the ends of others that run from

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⁷ E. B. Knopf and E. Ingerson: Structural Petrology. *Memoir No. 6*, Geol. Soc. Amer. (1938), 270 pp.

⁸ Andrade: Int. Conf. Physics (Phys. Soc. London) (1935) II, 173.

bottom to top, similar to some of those in Fig. 2 in the paper. His more widely spaced lines are complete. Of the incomplete lines, the farther one is removed from its complement coming from the opposite direction, the farther it runs past the terminus of the latter. All this, according to Andrade, is in confirmation of Taylor's^{9,10} theory of plastic deformation by fault migration under the influence of stress, since it agrees with the latter's calculations that the stress required to make one of two opposed lines run past the other varies inversely with the distance

between the lines. The greatest distance two lines can overlap without completely traversing the crystal is equal to the distance or spacing between them, of the order of 10^{-4} cm. In these respects Taylor's calculations, with the possible exception of the second, are confirmed as well by Fig. 2. This, however, does not necessarily constitute a general confirmation of his entire theory, as the phenomena noted by Andrade, and also shown here, may well be susceptible of other explanation as reasonable as that based upon dislocations in the crystal structure and the propagation thereof. The line discontinuities may be the effect of other kinds of local stress inhomogeneities.

⁹ Taylor: *Proc. Roy. Soc. London* (1934) **45-A**, 362.

¹⁰ Taylor: *Jnl. Inst. Metals* (1932) **48**, 227.

Bismuth—Its Effect on the Hot-working and Cold-working Properties of Alpha and Alpha-beta Brasses

BY WILLIAM B. PRICE,* MEMBER A.I.M.E., AND RALPH W. BAILEY†

(New York Meeting, February, 1942)

ARSENIC, antimony and phosphorus are now used in the brass industry as standard inhibitors in preventing dezincification in condenser tubes. This subject has been thoroughly covered by Barry,¹ who de-

antimony and bismuth are placed in group V-B and the type of crystal lattice for arsenic, antimony and bismuth is given as rhombohedral. The Metals Handbook³ lists them as "rhombohedral hexagonal,"

TABLE I.—Corrosion-test Data

Alloy No.	Composition ^a Per Cent			Tensile Strength, Lb. per Sq. In.			Elongation, Per Cent in 2 In.		
	Copper	Bismuth	Zinc	Original	After Immersion		Original	After Immersion	
					1 Week	2 Weeks		1 Week	2 Weeks
3a ^b	61.83		Bal.	50,000	28,600	28,500	60	37	26
638 ^b	60.26	0.08	Bal.	50,400	30,800	29,700	55	40	45
				54,000	25,000	^c	46	19	^c
640	60.00	0.25	Bal.	53,600	23,900		43	32	
				53,500	19,700	^c	45	13	^c
644	60.00	1.00	Bal.	53,000	19,900		48	9	
				48,100	23,900	^c	53	32	
				48,400	30,100		50	31	

^a Since check analyses indicated that all heats approached closely the nominal composition, each individual heat was not analyzed.

^b Heats that were analyzed.

^c These samples were so completely dezincified that tensile testing was impossible.

scribed the testing procedure by total immersion of suitable specimens in a 1 per cent cupric chloride solution at definite temperatures. Effects of dezincification were then determined by loss in tensile strength and elongation of the test specimens after definite periods of immersion.

In the crystallography of the chemical elements as tabulated by William Hume-Rothery,² phosphorus (metallic), arsenic,

with the additional notation that for arsenic this is the ordinary form at 20°C.; other modifications known or probable at other temperatures.

In view of these statements and of the fact that phosphorus, arsenic and antimony are effective in increasing the resistance to dezincification, it was natural to assume that bismuth would act in the same manner. A series of tests was therefore carried out employing the methods described by Barry. Much to our surprise, bismuth did not inhibit dezincification, but rather seemed to accelerate it. Tensile-test speci-

Manuscript received at the office of the Institute, Nov. 29, 1941. Issued as T.P. 1441 in METALS TECHNOLOGY, June 1942.

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¹ References are at the end of the paper.

mens, with a test section $2\frac{1}{2}$ by $\frac{1}{2}$ by 0.025 in. thick, machined from strips 6 by 1 by 0.025 in., were used in the corrosion tests. Statistical data are shown in Table 1.

In preparing samples containing the required amount of bismuth, it was noticed that the alpha-beta alloy seemed to cold-roll as well as the same alloy without the bismuth. Since this behavior was contrary to all references in the literature, it was decided to conduct a research to determine the effect of bismuth in varying amounts on the alpha and alpha-beta brasses.

A review of the literature revealed much work on the effect of bismuth on copper, but little, except by implication, on the effect of bismuth on brass. Archbutt and Prytherch⁴ summarize previous work, and add their own observations. They state that 0.01 per cent of bismuth, in the absence of oxygen or other corrective agents, makes copper hot short, and that 0.05 per cent of bismuth makes copper cold short. They also conclude that arsenic, antimony and oxygen tend to counteract hot shortness due to bismuth, but that phosphorus "did not appear to intensify the effect of bismuth."

Smithells,⁵ in referring to the effect of bismuth on the mechanical properties of brass, says, "For most purposes 0.005 per cent of bismuth is the maximum permissible, and where the metal is to undergo severe cold-work, this element should be excluded."

Jevons⁶ states that a very small percentage of bismuth in brass reduces the ductility of the metal to such an extent that working by ordinary methods becomes impossible, and that 0.005 per cent of bismuth is the most that can be present without causing serious trouble.

EXPERIMENTAL PROCEDURE AND RESULTS

Casting

Melting and alloying were carried out in clay-graphite crucibles in a high-frequency

induction furnace, using charcoal to cover the melt. Cast bars $\frac{3}{4}$ by $1\frac{5}{8}$ by 12 were used for the production of strip, and cast bolts $1\frac{3}{4}$ by 15 in. for the production of rod.

Cold-rolling

Little difficulty was experienced in cold-rolling 60-40 brass containing up to 3 per cent of bismuth. Initial reduction of annealed cast bars was limited to about 20 per cent. Reductions of 30 to 40 per cent were employed in subsequent processing, following suitable anneals.

Early attempts to cold-roll 70-30 brass containing 0.05 to 1 per cent bismuth met with little success. The addition of 0.01 to 0.02 per cent phosphorus to these alloys, however, overcame this difficulty.

In the earlier attempts to cold-roll alpha brass containing bismuth, it was observed that cracking became noticeable in the cold-rolling operation that followed an initial cold reduction of 20 per cent, and a 600°C. anneal. The possibility of "fire-cracking" during the anneal was considered, and the following series of tests was made to investigate this possibility and to observe the effect of variations in the copper content of the alloy.

Flat bars were made up of three alloys containing 1 per cent bismuth, with 61, 64 and 66 per cent copper, respectively. Variations in the rolling and annealing practice produced the following results: With a light initial reduction (20 per cent) followed by an anneal in a muffle previously heated to the annealing temperature, 600°C., the 64 and 66 per cent copper alloys showed fine surface cracks, after the anneal, while the 61 per cent copper alloy did not crack. With the same initial reduction, followed by an anneal in which the bars were placed in a cold muffle and heated slowly to 600°C., the 66 per cent copper alloy showed fine cracks after the anneal, while the 61 and 64 per cent copper alloys did not crack.

With the heavier initial reduction (30 per cent) followed by an anneal in which the bars were brought up to temperature slowly, none of these alloys showed cracks,

produce "fire-cracking" in leaded brasses will also produce cracking in alloys containing bismuth; these conditions being the presence of internal stresses due to

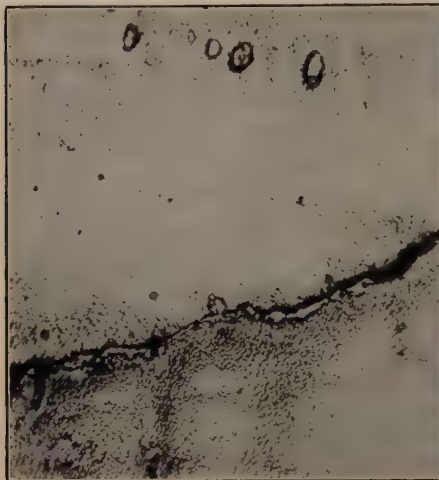


FIG. 1.—INTERCRYSTALLINE CRACK IN ALLOY CONTAINING 66 PER CENT COPPER, 1 PER CENT BISMUTH AND 33 PER CENT ZINC. $\times 100$.

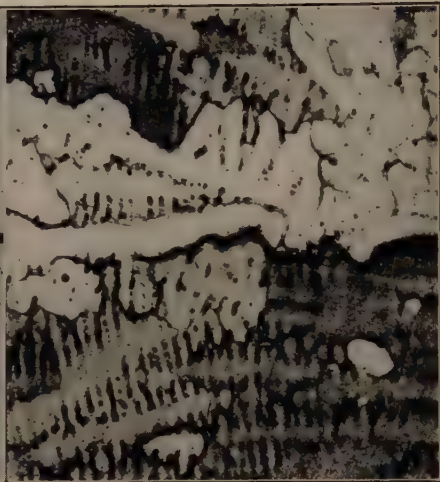


FIG. 2.—INTERCRYSTALLINE SEGREGATION IN ALLOY CONTAINING 66 PER CENT COPPER; 1 PER CENT BISMUTH AND 33 PER CENT ZINC. $\times 1000$.



FIG. 3.—FORGINGS.

Top, left to right: 60-40 brass + 0.06Bi; 60-40 brass + 2Pb, + 0.06Bi; 70-30 brass + 0.03Bi + 0.03P.

Bottom, left to right: 60-40 brass + 0.06Bi + 0.03P; 60-40 brass + 2Pb + 0.07Bi + 0.03P; 60-40 brass + 2Pb.

and all three were processed further without special precautions. These tests indicated that conditions that are known to

light reductions, and the sudden application of heat. Since careful examination of such bars before the anneal failed to

reveal any cracks, it was fairly evident that "fire-cracking" had occurred.

Further tests were made on an alloy containing 1 per cent bismuth, with 66 per cent copper, to determine the exact time of occurrence, and the nature of the cracks. Recrystallization had destroyed any direct microscopic evidence, in the above tests, that the cracks followed the crystal boundaries of the cast structure. One piece of this alloy, therefore, was given an initial cold reduction of 20 per cent, and was placed for 5 min. in a muffle previously heated to 600°C. Visual and microscopic examination failed to reveal cracks in the rolled bar before heating, but after the bar had been heated, as above, cracks were readily apparent. Photomicrographs, Figs. 1 and 2, show intercrystalline segregation, presumably of bismuth, and the intercrystalline path of the cracks found in this bar. The heating time was long enough to allow "fire-cracking" to take place but not long enough to bring about recrystallization. Thus direct evidence was obtained that cracking followed the crystal boundaries of the cast structure.

TABLE 2.—Alloys for Cold-rolling (See also Table 1)

Alloy No.	Composition, Per Cent			
	Copper	Bismuth	Phosphorus	Zinc
637	70	0.05		Bal.
639	70	0.25		Bal.
643	70	1.00		Bal.
646	70.13 ^a	0.05	0.01	Bal.
657	70.24 ^a	1.08	0.02	Bal.
681	61.38 ^a	1.04		Bal.
682	64.05 ^a	1.01		Bal.
683	66.00 ^a	1.07		Bal.
687	60.00	3.00		Bal.
692	57.67 ^a	5.07		Bal.
693	68.59 ^a	2.97		Bal.
673	99.791 ^a	0.144	0.045	
684	99.9	0.10		
685	98.6	1.00	0.04	

^a Heats that were analyzed.

Subsequently, using every precaution against fire-cracking in the initial stages of processing, a 70-30 brass containing

1 per cent bismuth was cold-rolled to strip 0.025 in. thick.

By substituting swaging for rolling, in the initial breakdown of cast bolts, followed by annealing and drawing, it was possible to produce rod or wire from a 60-40 brass containing 5 per cent bismuth, and from a 70-30 brass containing 3 per cent bismuth.

Flat bars made by adding 0.14 per cent bismuth and 0.045 per cent phosphorus to cathode copper could be cold-rolled with little difficulty. Similar bars containing 0.10 bismuth alone, or 1 per cent bismuth plus 0.04 per cent phosphorus, could not be cold-rolled.

Hot-working

Hot-forging tests were chosen to indicate the effect of additions of bismuth, and bismuth plus phosphorus, upon the hot-working properties of certain alloys shown in Table 3. Slugs for forging were cut from pieces of 0.937-in. rod, which were made from 1¾-in. cast bolts by cold-rolling and

TABLE 3.—Alloys for Hot-forging

Alloy No.	Composition, Per Cent				
	Copper	Bismuth	Lead	Phosphorus	Zinc
669	60.22 ^a	0.065			Bal.
670	60.25 ^a	0.072		0.028	Bal.
671	69.87 ^a	0.035		0.029	Bal.
227	59		2.0		Bal.
674	58.56 ^a	0.06	1.95		Bal.
675	59.20 ^a	0.07	2.07	0.029	Bal.
687	60.00	3.00			Bal.

^a Heats that were analyzed.

drawing. Slugs 1½ in. long were heated to 750°C. and forged into parts having a central pin of ⅜-in. diameter and ⅜ in. long, and a flat section of 1⅞-in. diameter and 0.200-in. thick, as shown in Fig. 3. Two 60-40 brasses containing 0.06 per cent bismuth, with and without 2 per cent lead, yielded forgings that were acceptable, but showed a tendency to crack around the outside edge of the "flash." These two alloys, fortified by the addition of 0.03

per cent phosphorus, yielded excellent forgings. A 70-30 brass containing 0.03 per cent bismuth and 0.03 per cent phosphorus, was not forgeable at temperatures from 750° to 850°C. Small pieces of a 60-40 brass containing 3 per cent bismuth were hammered flat at forging temperatures, and showed fair hot-working properties in comparison with a similar test on a standard 60-40 forging brass containing 2 per cent lead.

Machinability

To measure the effect of bismuth upon the relative machinability of Muntz metal, the test described by Kimberley⁷ was

TABLE 4.—*Machinability Tests*

Alloy No.	Composition, Per Cent				Relative Machinability
	Copper	Bismuth	Lead	Zinc	
202 ^a	62.52		2.59	Bal.	100 (Arbitrary Standard)
36	62.00			Bal.	35
642	60.00	0.5		Bal.	55
676 ^a	62.04	1.02		Bal.	87
677 ^a	61.38		1.04	Bal.	90
678 ^a	61.86	0.49	0.43	Bal.	87
687	60.00	3.00		Bal.	88

^a Heats that were analyzed.

employed. This test measures the rate of penetration of a standard flat drill turning at a constant speed, under a constant load.

The materials to be tested were in the form of flat bars $\frac{3}{8}$ in. thick, cold-rolled from $\frac{3}{4}$ -in. cast bars. Tests made parallel to the rolled surface, both parallel to and at 90° to the direction of rolling, showed no appreciable variation within the bar. Test results are given in Table 4.

Physical Properties, Ductility

One strip of 2-1 brass containing 1 per cent of bismuth was tested in comparison with common high brass, with the results shown in Table 5.

CONCLUSIONS

1. Dezincification of Muntz metal is not inhibited by additions of bismuth, but seems to be somewhat accelerated.

2. Alpha-beta brasses containing up to 3 per cent bismuth may be cold-rolled with little difficulty by standard commercial practice. A 60-40 brass containing 5 per cent bismuth can be fabricated by using a special technique described in the foregoing pages.

3. The cracking encountered in cold-rolling and annealing alpha brass containing bismuth is a type of "fire-cracking." This type of cracking may be avoided by using a suitable rolling and annealing schedule, or by additions of 0.01 to 0.02 per cent phosphorus, in alloys containing up to 70 per cent copper and 1 per cent bismuth. Fire-cracking was found to occur in the anneal following the initial cold-reduction of a cast bar, but was not likely to occur in subsequent anneals. A 70-30 brass containing 3 per cent bismuth could be fabricated using a special technique described herein.

4. Additions of 0.05 per cent bismuth impair very slightly the hot-forging properties of alloys containing 60 per cent copper, with or without 2 per cent lead. The addition of 0.03 per cent phosphorus restores the excellent hot-working properties of these alloys.

A 60-40 brass containing 3 per cent bismuth showed fairly good hot-working properties.

TABLE 5.—*Physical Tests—Ductility*

Alloy No.	Composition, Per Cent			Gauge, In.	Grain Size, Mm.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent in 2 In.	Erichsen Value, Mm.
	Copper	Bismuth	Zinc					
683 ^a	66.00	1.07	Bal.	0.025	0.035	50,300	54	10.8
203 ^a	66.12		Bal.	0.025	0.035	50,800	62	11.0

^a Heats analyzed.

5. The effect of additions of bismuth up to 1 per cent upon the machinability of Muntz metal is comparable to that of lead. No additional improvement was observed with 3 per cent bismuth.

6. The ductility of common high brass sheet, as measured by elongation and Erichsen cup test, is impaired very little by the addition of 1 per cent bismuth.

7. Copper containing 0.14 per cent bismuth plus 0.045 per cent phosphorus may be cold-rolled with little difficulty. Attempts to cold-roll copper containing 0.10 per cent bismuth alone, or 1 per cent bismuth plus 0.04 per cent phosphorus, were unsuccessful.

ACKNOWLEDGMENTS

The assistance of Mr. F. M. Barry and Mr. W. D. France, in chemical and spectrographic analyses, respectively, is gratefully acknowledged.

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DISCUSSION

(D. K. Crampton presiding)

J. S. SMART, JR.* AND A. A. SMITH, JR.* Barber, N. J.—Messrs. Price and Bailey, with the help of a few astronomical bismuth contents, have laid an old ghost to rest as far as certain brasses are concerned. Unfortunately, as indicated by the authors' data, the tolerance of copper for bismuth is considerably lower. At the risk of destroying a comfortable scapegoat, and of becoming involved in a discussion where no quarter is shown, the writers venture to offer some observations on the effect of varying

amounts of bismuth on the hot-working and cold-working properties of high-purity copper, with the hope that they will serve to amplify the coverage of the present paper.

The experiments cover the behavior of both oxygen-free and oxygen-bearing alloys. The former condition was obtained by continuously casting $\frac{3}{8}$ -in. rod, and the latter by remelting portions of the rod and pouring through air into a slug mold 1 in. in diameter by 8 in. long. Test wires of 0.081-in. diameter were to be prepared from the oxygen-free rods by three reductions of about 30 per cent followed in each case by an intermediate anneal for $\frac{1}{2}$ hr. at 600°C., and then a 75 per cent cold reduction to size. Alloys containing 0.0001 per cent, 0.0005 per cent, and 0.001 per cent Bi were processed in this manner without difficulty. Both the 0.005 per cent and 0.01 per cent Bi samples were readily reduced 30 per cent from the chill-cast rod, but exhibited marked brittleness after annealing at 600°C. The same rods were rendered ductile by heating to 850°C. for 1 hr. and quenching, and were again drawn 30 per cent. It was found that the brittle condition could be obtained at will after any sequence of operations, simply by annealing at 600°C., but that good wire containing as high as 0.05 per cent Bi could be produced by using the 850°C. quench.

This behavior obviously is not due to fire cracking, but very probably indicates a large increase in the solid solubility of bismuth at higher temperatures. Inasmuch as the effect of soluble bismuth on the conductivity is negligible, the solubility changes cannot be confirmed by resistivity measurements on heat-treated samples, but, as will be pointed out later, other observations confirm this premise.

The oxygen-bearing slugs were heated to 850°C. and directly hot-rolled to $\frac{5}{16}$ -in. rod in nine passes without reheating. No difficulties of any kind were encountered with any of the samples containing 0.005 per cent Bi or less, and these rods were drawn to wire using the 600°C. anneal without the appearance of cracks or other tendency toward brittleness. The slug containing 0.01 per cent Bi left the furnace at 850°C. and was rolled at a bright red heat through five passes without cracking. As it cooled through the last four passes to a temperature of approximately 600°C. many fine cracks appeared, and the final rod was very cold-short. After quenching from 1 hr. at 850°C.

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the ductility was restored and reasonably good wire was produced, although slivers were common.

The oxygen contents of the samples varied from 0.023 to 0.037 per cent O_2 , and it is apparent from the behavior of the 0.005 per cent Bi samples that oxygen has nullified part of the effect of bismuth, as has been noted by most previous observers. Evidently, at least part of the bismuth is removed from solution as an oxide, but the reaction does not appear to be complete, and the stability of the oxide formed is questionable.

Certainly, the most reasonable interpretation of the effect of bismuth in producing cracking in copper rests on the premise that soluble bismuth has little if any effect; that an appreciable solid solubility exists at 850°C., permitting accommodation of considerably more bismuth than many previous observers were willing to concede; that precipitation (probably at the grain boundaries) results in the appearance of a low-temperature (circa 600°C.) embrittlement range, which may or may not be due to the presence of molten Bi or Bi_2O_3 at the grain boundaries.

C. S. SMITH,* Waterbury, Conn.—The authors are to be congratulated on having provided one more example of an impurity, hitherto regarded as anathema, that actually is not particularly harmful under certain conditions. They would, however, be doing the brass industry a disservice if they caused the widespread adoption of the idea that bismuth is not under certain conditions—indeed under most commercial ones—quite as undesirable as has hitherto been supposed.

It is indeed true that bismuth can be tolerated in large amounts in 70-30 cartridge brass, provided that the alloy is to be cold-rolled, and provided that it can be annealed with care. On the other hand, an increasing amount of alpha brass is being hot-rolled, and in the hot-rolling mill bismuth certainly deserves its unsavory reputation. Experiments we have recently carried out on a laboratory scale show that 70-30 brass containing 0.006 per cent Bi or more failed miserably on hot-rolling at any reasonable temperature. This was true regardless of whether the brass had been deoxidized with phosphorus or not. It is obvious, therefore,

that all material reaching the casting shop for the fabrication of cartridge brass must be free from bismuth, whether this is virgin metal or scrap, and it is undesirable to allow more than the present limits of bismuth impurity in the virgin metals unless the scrap therefrom can be most carefully segregated.

We have confirmed the authors' finding regarding the effect of deoxidation; though, like the authors, we have no theory to account for it. Working with small laboratory castings 5 by $1\frac{1}{4}$ by $\frac{5}{8}$ in., we found that 70-30 brass with bismuth up to 1 per cent could be cold-rolled at least 50 per cent reduction from the casting if it had been deoxidized with 0.03 per cent phosphorus, while similar castings not deoxidized cracked after rolling about 45 per cent if they had contained 0.16 per cent or more bismuth. Castings rolled 30 per cent reduction and then annealed at 600°C. always fire-cracked if they contained bismuth (0.009 to 1.0 per cent), even though they were slowly heated with the furnace. No fire-cracking was observed in deoxidized material under similar conditions.

By way of confirmation of the authors' tests, some tensile properties are shown in Table 6, This material, of the composition shown, was fabricated by rolling from the small castings mentioned above by rolling from 0.625 to 0.05 in., with intermediate anneals at 0.32, 0.20 and 0.10-in. gauge. All anneals were at 600°C., the specimens being heated with the furnace.

It is obvious that bismuth in the amounts indicated has virtually no effect on either the yield or tensile strength or the elongation of 70-30 brass. The machinability is improved but no more so than can be done with the usual addition for this purpose—lead.

The contribution to the discussion by Mr. A. A. Smith, Jr., regarding brittleness of bismuth-bearing copper, is of great interest. It should be noted in this connection that Clement Blazey as long ago as 1931¹¹ drew what amounted to a solubility diagram of bismuth in copper by plotting the temperature of loss of hot-shortness against bismuth content for a series of alloys. In principle, Blazey's method is exactly that now being used in several laboratories for the determination of solidus temperatures by deformation tests.

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¹¹ C. Blazey: Brittleness in Copper. *Jnl. Inst. Metals* (1931) 46, 353-381.

H. L. BURGHOFF,* Waterbury, Conn.—The authors indicate that phosphorus is of considerable effect in overcoming embrittlement produced by bismuth alone. It is indicated, therefore, that there may be other elements that act in the same manner. Along this line, Tour¹² reported several years ago on the characteristics of certain copper-silicon alloys, which contained from about 1 to 5 per cent bismuth. These were stated to be highly machinable, owing to the presence of bismuth, and also to be ductile.

alpha brasses, both quenched and cooled from the hot-working temperatures, from the viewpoint of determining the distribution and correlating this with the tendency to fire-crack? Also, has any such investigation been made on the effect of additions of bismuth or phosphorus on the lead distribution in the alloys investigated for hot-forging properties?

R. W. BAILEY.—We feel somewhat encouraged by Dr. Smith's confirmation of our results and I think that we would agree with him that we cannot let bismuth run loose in a

TABLE 6.—*Tensile Properties of 70-30 Brass Containing Bismuth*

Alloy No.	Composition by Analysis, Per Cent					Yield Strength, Lb. per Sq. In.		Tensile Strength, Lb. per Sq. In.		Elongation, Per Cent in 2 In.	
	Copper	Zinc	Bismuth	Phosphorus	Lead	6 B. and S. Numbers Hard	Annealed 1 Hr. 600°C.	6 B. and S. Numbers Hard	Annealed 1 Hr. 600°C.	6 B. and S. Numbers Hard	Annealed 1 Hr. 600°C.
4371	70.06	29.94	0.0	0.0		67,500	12,500	87,600	45,900	6.50	62.0
4371D	70.43	29.54		0.027		64,100	12,800	88,400	46,300	7.0	60.0
4372	69.96	30.03	0.009			69,100	12,900	87,400	46,300	6.0	68.5
4372D	70.29	29.67	0.010	0.027		64,000	12,200	87,600	46,900	5.0	74.0
4373	69.99	29.96	0.05			65,900	12,900	86,300	45,800	3.5	60.5
4373D	70.26	29.67	0.04	0.026		64,000	12,000	87,500	46,600	6.0	70.5
4376	71.02	28.94	0.04	"		65,700	12,800	87,600	46,400	5.0	67.0
4374	69.98	29.86	0.16				^b				
4374D	70.32	29.46	0.19	0.027		64,800	12,000	87,600	46,800	5.5	71.0
4375	70.17	28.90	0.93				^b				
4375D	70.42	28.58	0.97	0.027		63,100	12,800	87,300	46,200	5.0	63.0
4395	70.03	29.88	0.04		0.05		^b				
4395D	70.30	29.58	0.05	0.027	0.04	65,400	13,000	87,100	46,700	5.0	67.0

^a No phosphorus addition; cast out of contact with air.

^b Bar cracked on rolling about 45 per cent reduction from the casting.

Another point I want to bring up is the effect of annealing temperature. The work by Blazey on bismuth-bearing copper has been referred to by Dr. C. S. Smith. Mr. A. A. Smith has checked that work in his laboratory. Work that we have recently carried out on some bismuth-bearing brasses with bismuth contents of about 0.01 per cent and less indicates that the brittleness can be made to appear and disappear according to the annealing treatment. It is quite similar to the effect in copper. For high annealing temperatures, such as 700°C., these brasses are quite ductile. If subsequently or previously annealed in the range from 400° to 500°C., they are very distinctly brittle, failing in the tensile test with intergranular fractures.

R. G. TREUTING,† New Haven, Conn.—Has any microscopic investigation been made of the distribution of bismuth in alpha plus beta and

brass mill. However, we attempted to show that under certain conditions, and perhaps with very careful control of scrap copper containing bismuth, this could be used in the industry.

In answer to Dr. Burghoff's question, the effect of other deoxidizers was tried in a small scale. We found there was no addition with the addition of silicon, calcium, aluminum, or silicon deoxidizers. We also found that anneals up to 750° were not effective in preventing this intercrystalline brittleness.

In answer to Mr. Treuting, such microscopic examinations as we made did not indicate that there was any preferred segregation of bismuth in either the alpha or beta. As we tried annealing and quenching this alpha-beta alloy from different temperatures and could not find any pronounced difference in the distribution of bismuth, we felt that perhaps the addition of phosphorus dispersed the bismuth more finely and we hope that it prevented segregation at the grain boundaries, although we were not able to prove that.

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¹² U. S. Patent 1959509.

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Directional Properties of 68-32 Brass Strip

By H. L. BURGHOFF,* MEMBER A.I.M.E., AND E. C. BOHLEN†

(New York Meeting, February 1942)

THE work reported in this paper was carried out to supplement the existing information concerning directional properties and recrystallization textures of annealed brass sheet and strip. These characteristics are of direct interest when the forming and drawing properties of such material are being considered. Among those who have made contributions in this field are Bass and Glocker;¹ Bauer, Göler and Sachs;² Phillips and Samans;³ Pratt;⁴ Price;⁵ Cook;⁶ Richards;⁷ Brick;⁸ and Brick and Williamson.⁹

These investigators have found, in general, that in brass strip that shows directional variations in properties, tensile strength has a minimum value and elongation has a maximum value at 45° to the rolling direction. The most pronounced directional properties have been found in material given the greatest reductions in rolling followed by high annealing temperatures. Recrystallization texture of brass has been variously reported as (113)[112], (001)[100], and a combination of (110)[115] and traces of the primary rolling texture, (110)[112].

The directional studies have been very informative, but actual tests appear to have been confined to material in its final condition. Tests at intermediate stages have received little attention although previous history of some materials has been partly considered. Perhaps the most comprehensive investigation was made by

Cook,⁶ who studied the directional properties of 70-30 brass strip for which the final and penultimate, or next to the last, anneals and the final reductions were varied. He found that, for any given combination of penultimate anneal and final reduction, the tendency toward the development of directional properties was reduced as the temperature of the final anneal was decreased. In addition to drawing cups and making tensile tests of the finished material at various angles to the rolling direction, he measured the frequency and the angles of twins in grains for several specimens. Plots of his twin counts showed directionality for the materials that produced eared cups.

TEST MATERIALS AND EQUIPMENT

For this investigation, one commercial heat of 68-32 brass was cast in the form of bars for cold-rolling, 13½ in. wide and 1½ in. thick. The analysis was as follows: 68.83 per cent copper, 0.04 per cent lead, 0.01 per cent iron, 31.12 per cent zinc (by difference).

The bars were so processed to the final thickness, 0.020 in., as to obtain on this thickness all possible combinations of the variables listed below except those involving the sequence of 84 per cent penultimate reduction and 84 per cent final reduction:

1. Penultimate reductions of 37 per cent, 50 per cent and 84 per cent;
2. Penultimate anneals at 800°, 900°, 1050° and 1200°F.;
3. Final reductions of 37 per cent, 50 per cent, 69 per cent and 84 per cent;

Manuscript received at the office of the Institute July 26, 1941. Issued as T.P. 1420 in METALS TECHNOLOGY, January 1942.

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¹ References are at the end of the paper.

4. Final anneals at 800°, 900°, 1050° and 1200°F.

Material for testing on 0.020 in., as on the other test gauges, was in the annealed condition. The bars were sawed in half lengthwise after the first reductions were made, so that the later heavy reductions could be made easily. In processing the metal to the thicknesses previous to the penultimate thicknesses or gauges, only three different rolling schedules were necessary, which were as shown in the accompanying table.

Rolling Gauges

1½" (33 %)	1.000" (50 %)	0.500" (48 %)	0.258"*
1½" (50 %)	0.128"* (50 %)	0.064"*	
1½" (47 %)	0.800" (50 %)	0.400" (49 %)	0.204"*
1½" (50 %)	0.102" (50 %)	0.051"	
1½" (50 %)	0.750" (51 %)	0.365"* (50 %)	0.182"
(55 %)	0.081"*		

* These gauges are previous to penultimate gauge.

Breaking down and intermediate anneals were made in mill furnaces at about 1100°F., while the penultimate and final anneals were made in a laboratory furnace for periods of one hour.

Suitably calibrated hydraulic testing machines were used in the tensile testing. Stress-strain curves were obtained with a Templin-type automatic recorder. A dial gauge, reading accurately to 0.001 in., was arranged for measurement of ears on drawn cups.

TEST PROCEDURE

The only test made on the gauges immediately previous to the penultimate gauges was determination of grain size. On the penultimate gauges, 0.032 in., 0.040 in., 0.064 in. and 0.128 in., Rockwell hardness and grain size were determined, as were tensile strength and elongation for specimens cut at 0°, 22½°, 45°, 67½° and 90° to the rolling direction. Tensile tests were made in triplicate.

Numerous tests were made on the final gauge, 0.020 in. Cups were drawn for each material, blank diameter being 3 in., cup diameter 1.75 in. and average cup height 1.25 in. Unevenness or earing of the cups

was carefully measured for at least three cups per material. Microstructures of the annealed metal were examined for sections parallel to the rolling surface. Tensile strength and elongation of selected materials were obtained, representing all previous reductions and the extremes of annealing. Some of these tests were made at 0°, 45°, and 90° to the rolling direction while others were made at 0°, 22½°, 45°, 67½° and 90°. Several materials whose cups had six ears at 0° and 60° to the rolling direction were subjected to tensile tests at these angles as well as at 30° and 90°.

Stress-strain curves to fracture were made upon several typical materials for correlation with ordinary tensile tests. The curves from 0 to about 0.5 per cent extension were made with the stress-strain recorder, while the curves from this point to fracture were obtained by the use of dividers set for definite increments of strain.

X-ray analyses for the determination of the recrystallization texture of two materials whose cups had four and six ears, respectively, were made by Dr. R. M. Brick, of Yale University. Diffraction patterns were obtained for four other materials, to give some indication of the degree of preferredness.

DISCUSSION OF RESULTS

The grain sizes for the gauges previous to the penultimate gauges are included in Table 1 and range from 0.045 to 0.065 mm. in average diameter. Of the 11 different conditions, only two had grain sizes that were reported to be less than 0.055 mm., so that the properties of the metal at this point might be expected to be quite uniform.

Grain size and Rockwell hardness values for the penultimate gauges as annealed at 800°, 900°, 1050° and 1200°F., following penultimate reductions of 37 per cent, 50 per cent and 84 per cent, are also given in Table 1. Hardness appears to be inde-

TABLE 1.—*Grain Sizes on Previous, Penultimate and Final Gauges and Rockwell Hardness on Penultimate Gauge*

Previous		Penultimate						Final					
Gauge, In.	Grain Size, Mm.	Reduction, B. and S. Nos.	Gauge, In.	An- neal, Deg. F.	Grain Size, Mm.	Rockwell Hardness		Reduction, B. and S. Nos.	Grain Sizes for Given Anneals, Mm.				
						F	B		800°F.	900°F.	1050°F.	1200°F.	
0.050	0.050	4	0.032	800	0.025	75	31	4	0.020	0.030	0.060	0.090	
		4	0.032	900	0.035	71	23	4	0.020	0.035	0.055	0.100	
		4	0.032	1050	0.065	60	5	4	0.025	0.030	0.055	0.100	
		4	0.032	1200	0.085	55		4	0.030	0.035	0.065	0.100	
0.064	0.055	6	0.032	800	0.015	79	38	4	0.017	0.025	0.050	0.100	
		6	0.032	900	0.025	72	26	4	0.020	0.025	0.050	0.100	
		6	0.032	1050	0.055	63	10	4	0.025	0.030	0.060	0.100	
		6	0.032	1200	0.090	53		4	0.035	0.035	0.060	0.110	
0.200	0.065	16	0.032	800	0.008	89	56	4	0.015	0.035	0.055	0.100	
		16	0.032	900	0.020	76	34	4	0.020	0.030	0.065	0.100	
		16	0.032	1050	0.045	66	18	4	0.030	0.035	0.045	0.100	
		16	0.032	1200	0.075	58		4	0.030	0.040	0.055	0.110	
0.064	0.055	4	0.040	800	0.020	76	33	6	0.017	0.030	0.050	0.090	
		4	0.040	900	0.025	76	34	6	0.020	0.030	0.055	0.090	
		4	0.040	1050	0.040	63	10	6	0.017	0.030	0.050	0.090	
		4	0.040	1200	0.090	53		6	0.020	0.030	0.050	0.100	
0.083	0.065	6	0.040	800	0.010	84	47	6	0.017	0.025	0.055	0.100	
		6	0.040	900	0.025	74	30	6	0.020	0.030	0.045	0.100	
		6	0.040	1050	0.040	64	12	6	0.025	0.030	0.060	0.120	
		6	0.040	1200	0.085	55		6	0.025	0.030	0.055	0.120	
0.258	0.065	16	0.040	800	0.008	89	55	6	0.012	0.030	0.045	0.090	
		16	0.040	900	0.020	76	34	6	0.017	0.030	0.050	0.080	
		16	0.040	1050	0.045	63	9	6	0.020	0.030	0.045	0.110	
		16	0.040	1200	0.080	56		6	0.030	0.040	0.060	0.100	
0.104	0.065	4	0.064	800	0.015	79	38	10	0.015	0.020	0.055	0.100	
		4	0.064	900	0.020	74	29	10	0.017	0.025	0.060	0.100	
		4	0.064	1050	0.050	63	6	10	0.017	0.025	0.060	0.120	
		4	0.064	1200	0.090	50		10	0.017	0.025	0.060	0.120	
0.128	0.065	6	0.064	800	0.008	83	46	10	0.015	0.030	0.050	0.100	
		6	0.064	900	0.020	75	30	10	0.017	0.025	0.050	0.100	
		6	0.064	1050	0.045	65	15	10	0.020	0.030	0.060	0.100	
		6	0.064	1200	0.080	56		10	0.017	0.030	0.060	0.120	
0.363	0.045	16	0.064	800	0.010	82	44	10	0.017	0.020	0.045	0.080	
		16	0.064	900	0.025	75	31	10	0.017	0.025	0.045	0.090	
		16	0.064	1050	0.035	70	22	10	0.025	0.025	0.045	0.090	
		16	0.064	1200	0.085	53		10	0.020	0.025	0.055	0.100	
0.200	0.065	4	0.128	800	0.020	78	36	16	0.012	0.025	0.050	0.100	
		4	0.128	900	0.030	72	22	16	0.017	0.025	0.050	0.090	
		4	0.128	1050	0.045	62	8	16	0.012	0.025	0.065	0.100	
		4	0.128	1200	0.090	53		16	0.015	0.020	0.065	0.100	
0.258	0.065	6	0.128	800	0.010	75	48	16	0.015	0.030	0.045	0.080	
		6	0.128	900	0.025	74	29	16	0.015	0.030	0.050	0.080	
		6	0.128	1050	0.050	63	8	16	0.020	0.030	0.050	0.100	
		6	0.128	1200	0.075	58		16	0.020	0.025	0.050	0.100	

pendent of previous reductions and any preferred orientation at this stage, and is dependent only upon grain size. There was a tendency for grain size for a given anneal to decrease as the previous reduction increased, this effect being more noticeable for the thinner gauges and the lower annealing temperatures.

The directional properties for all penultimate gauges are shown in Fig. 1. Directionality of 0.128-in. material, as indicated by variation in tensile strength and elongation at the several angles to the rolling direction; increased as annealing temperature increased. There was little difference between previous reductions of

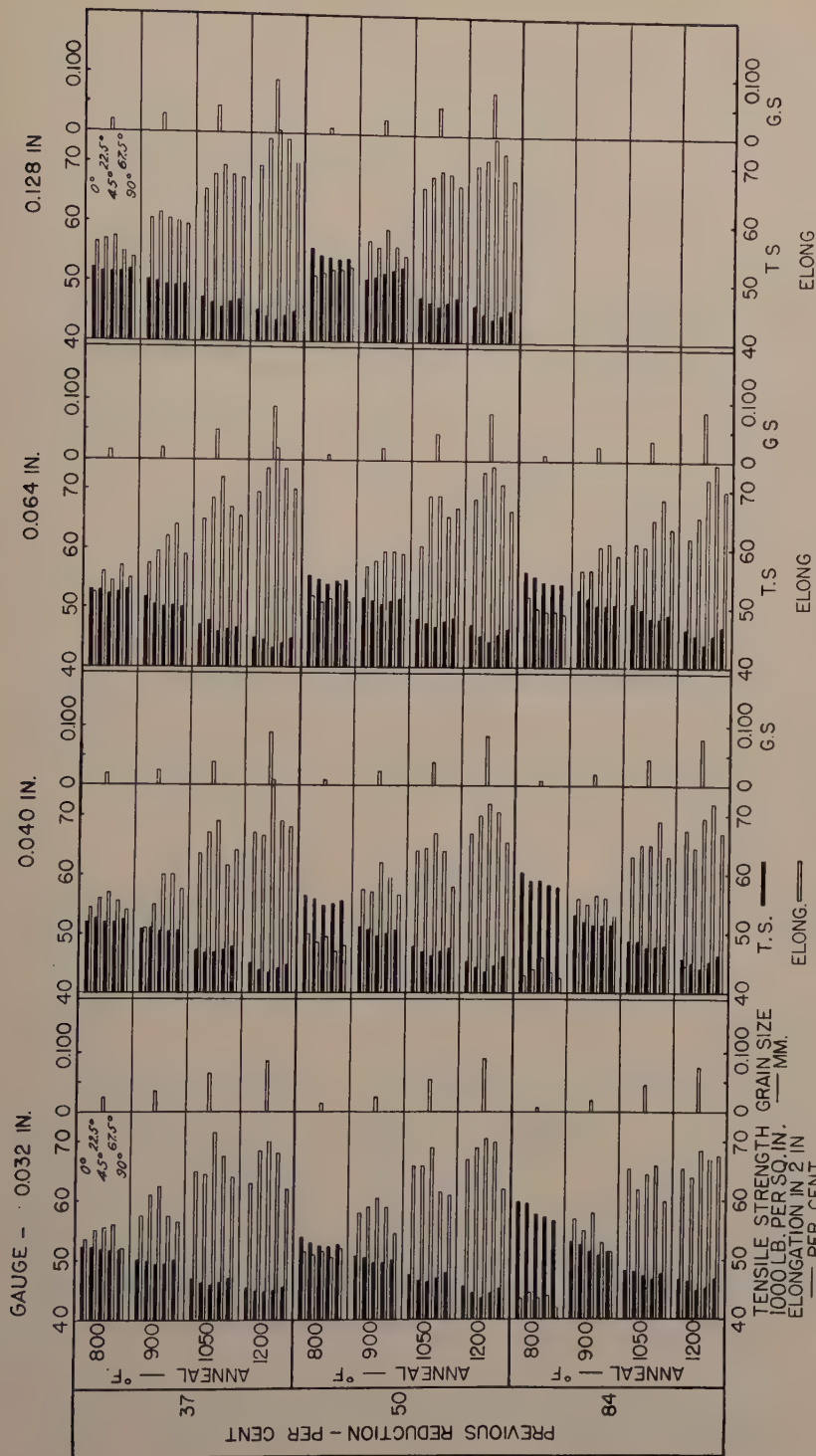


FIG. 1.—PROPERTIES OF MATERIALS FOR PENULTIMATE ANNEALS.

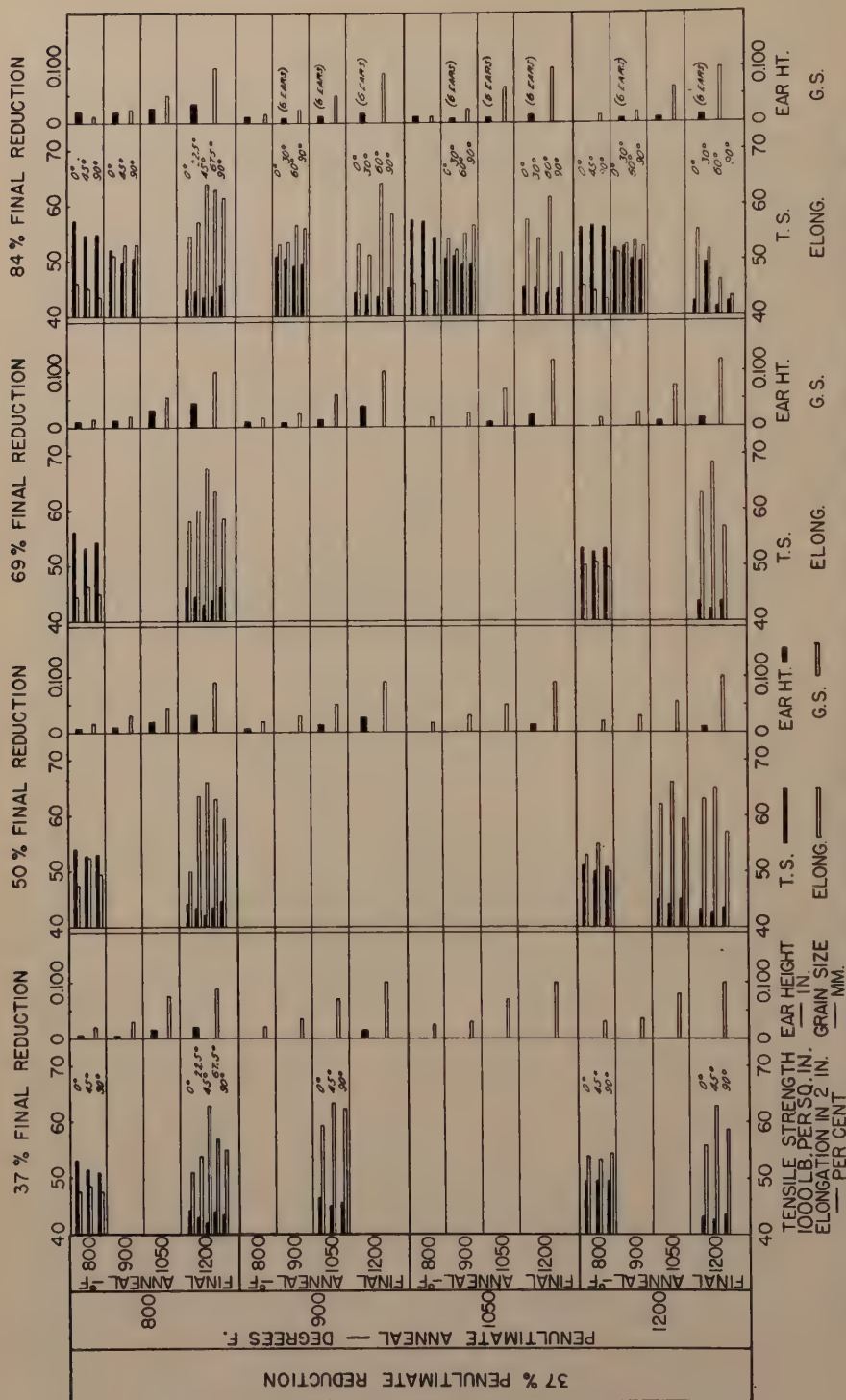


FIG. 2.—PROPERTIES OF ALL FINISHED MATERIALS (ANNEALED ON 0.020 INCH) GIVEN PENULTIMATE REDUCTION OF 37 PER CENT. Absence of value for ear height indicates no earing of cups. Tensile strength and elongation values absent for items not so tested.

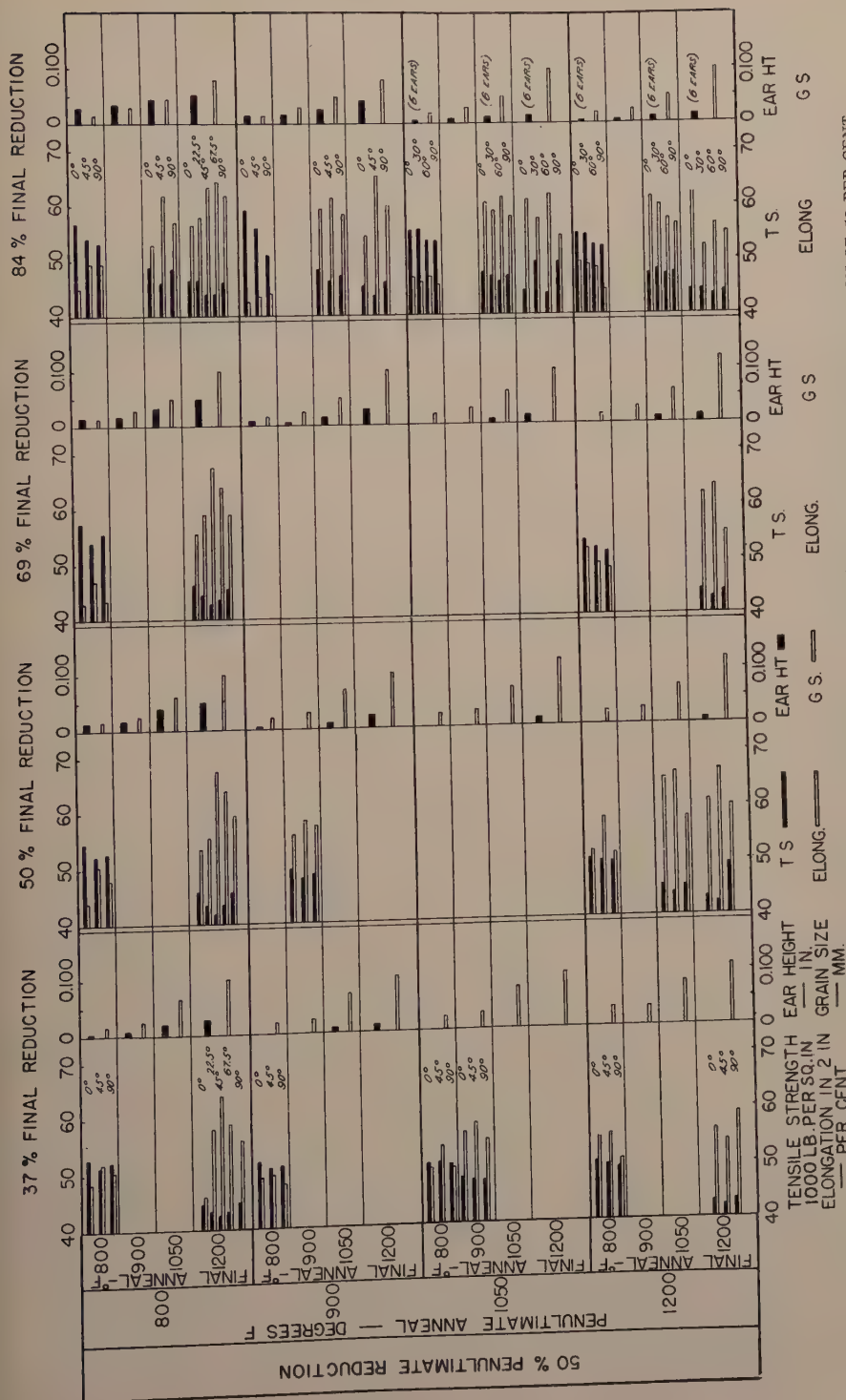


FIG. 3.—PROPERTIES OF ALL FINISHED MATERIALS (ANNEALED ON 0.020 INCH) GIVEN PENULTIMATE REDUCTION OF 50 PER CENT. Absence of value for ear height indicates no earing of cups. Tensile strength and elongation values absent for items not so tested.

37 and 50 per cent. As annealed at 1050°F. and 1200°F., tensile strength was minimum and elongation was maximum at 45° to the rolling direction. There was little

rolled 84 per cent there was some tendency for maximum elongation to be at 67½° to the rolling direction. Metal on 0.040 in. and 0.032 in. was similar to that on 0.064 in.

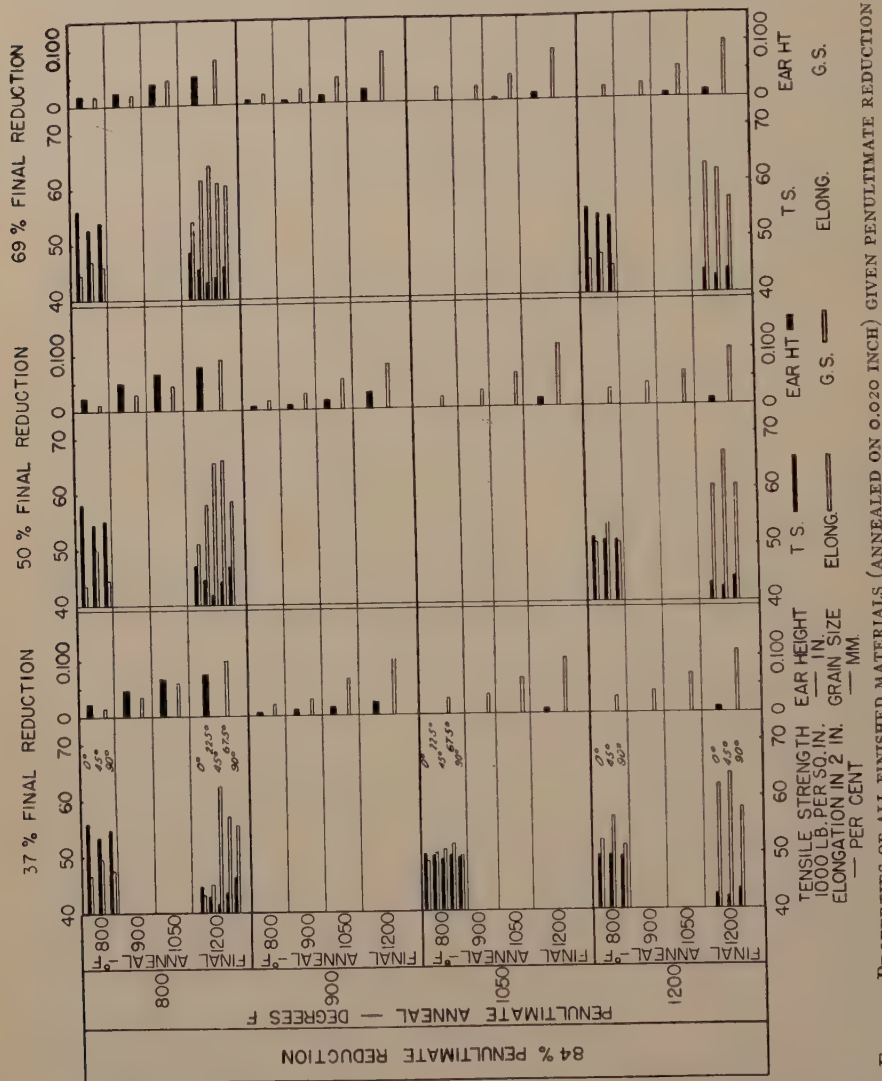


FIG. 4.—PROPERTIES OF ALL FINISHED MATERIALS (ANNEALED ON 0.020 INCH) GIVEN PENULTIMATE REDUCTION OF 84 PER CENT.
(Absence of value for ear height indicates no earing of cups. Tensile strength and elongation values absent for items not so tested.)

variation in directional properties as annealed at 800° and 900°F. Similar results were obtained for 0.064-in. metal. Material previously rolled 84 per cent was not greatly different from that rolled 37 and 50 per cent, although in metal previously

In all these tests, metal previously rolled 84 per cent gave more irregular directional results than for 37 and 50 per cent reductions, probably because of differences in preferred orientation, as will be discussed for the final gauge.

Grain sizes for the various annealed conditions on the final gauge, 0.020 in., are shown in Table 1 and in Figs. 2, 3 and 4. As on the penultimate gauges, grain size has a tendency to decrease for a given anneal as the previous reduction increases. This is further modified by the tendency of the grain size for a given anneal to increase as the previous annealing temperature or grain size increases.

Figs. 2, 3 and 4 also show tensile strength and elongation results for the final gauge, as well as the height of ears on the drawn cups. Most of the cups showing earing had four ears at 45° to the rolling direction. Cups drawn from several materials that had been finally rolled 84 per cent had six ears, which occurred at 0° and 60° to the rolling direction. The tendency to ear increased with penultimate reduction, with final reduction, as penultimate annealing temperature decreased, and as final annealing temperature increased. It increased as the final annealing temperature became increasingly greater than the penultimate annealing temperature.

Considering the complete history of the materials, there would appear to be a tendency for more strongly preferred orientations occurring at any point to be removed by subsequent rolling and annealing, while random or weakly preferred orientations may become more strongly preferred by rolling and annealing. Thus, directionality of the materials as given penultimate anneals at 800° and 900°F. is probably at a minimum on the penultimate gauge, for the preceding anneal was at about 1100°F., but is definitely greater for penultimate anneals at 1200°F. As subsequently and finally rolled and annealed, directionality after the 800° and 900°F. penultimate anneals is greater than after the 1200°F. penultimate anneal.

Table 2 gives a particularly clear idea of the conditions governing earing tendencies and shows that there are numerous combinations of reductions and anneals

in the present schedule which give no ears. Roughly these are: 800°F. to 1050°F. final anneals, 37 and 50 per cent final reductions, 1050° and 1200°F. penultimate anneals. Examination of the grain size values for these conditions indicates that the penultimate grain size should be equal to or greater than the final grain size to avoid earing in drawn cups. Final reduction of 69 per cent narrows the field and 84 per cent final reduction makes it almost impossible to avoid earing. Ear heights for the 84 per cent final reductions are not extreme, however, and are exceeded for some items with 84 per cent penultimate reductions and 800° and 900°F. penultimate anneals.

Directionality results, as indicated by tensile strength and elongation values at various angles to the rolling direction (Figs. 2, 3 and 4), are in good agreement with the cupping tests; i.e., elongation is maximum when tensile strength is minimum and ears occur at these positions. Conversely, the troughs between the ears are at points of maximum tensile strength and minimum elongation.

The extent of the earing on cups is roughly proportional to the differences in directional properties (strength and elongation) of the annealed stock used for cupping. There is no sharp division in directional properties for marginal cases whereby one can predict the occurrence of ears on cups from a knowledge of the directional properties of the material. When ears do occur, however, appreciable differences in directional properties seem always to exist.

The four ears on any one cup were naturally of consistent height, being symmetrical with the rolling direction. The troughs between the ears were also essentially unaffected by their relation to the rolling direction, although the tensile properties at 0° and 90° were often different. As finally annealed at 800°F., and probably for 900° and 1050°F. also, the strength at 0° is slightly higher on the whole

TABLE 2.—*Formation of Ears on Cups Drawn from 68-32 Brass Strip (0.020 Inch Gauge)*
 Blank diameter = 3 in.; cup diameter = 1.75 in.; Cup height = 1.25 in. Decimal figures indicate average height of ears in inches. Blank spaces indicate absence of ears. Four ears at 45° to rolling direction except as noted.

Penultimate		Final				
Reduction, Per Cent	Anneal, Deg. F.	Reduction, Per Cent	Anneal, Deg. F.			
			800°	900°	1050°	1200°
37	800	37	0.006	0.005	0.014	0.021
37	900	37				0.014
37	1050	37				
37	1200	37				
50	800	37	0.006	0.009	0.020	0.027
50	900	37			0.009	0.014
50	1050	37				
50	1200	37				
84	800	37	0.024	0.048	0.067	0.075
84	900	37	0.007	0.011	0.016	0.024
84	1050	37				0.009
84	1200	37				0.010
37	800	50	0.008	0.010	0.018	0.031
37	900	50	0.007		0.014	0.027
37	1050	50				0.013
37	1200	50				0.010
50	800	50	0.015	0.018	0.040	0.051
50	900	50	0.005		0.011	0.024
50	1050	50				0.013
50	1200	50				0.010
84	800	50	0.024	0.050	0.067	0.079
84	900	50	0.007	0.009	0.018	0.031
84	1050	50				0.015
84	1200	50				0.011
37	800	69	0.011	0.013	0.031	0.043
37	900	69	0.010	0.008	0.014	0.037
37	1050	69			0.009	0.020
37	1200	69			0.010	0.016
50	800	69	0.015	0.018	0.033	0.050
50	900	69	0.009	0.007	0.016	0.030
50	1050	69			0.009	0.016
50	1200	69			0.011	0.014
84	800	69	0.019	0.024	0.039	0.051
84	900	69	0.007	0.006	0.014	0.024
84	1050	69			0.006	0.012
84	1200	69			0.008	0.012
37	800	84	0.021	0.019	0.028	0.035
37	900	84	0.012	0.010 ^a	0.013 ^a	0.018 ^a
37	1050	84	0.012	0.008 ^a	0.010 ^a	0.014 ^a
37	1200	84		0.009 ^a	0.010 ^a	0.013 ^a
50	800	84	0.028	0.035	0.045	0.053
50	900	84	0.016	0.017	0.028	0.043
50	1050	84	0.007 ^a	0.009 ^a	0.012 ^a	0.015 ^a
50	1200	84	0.006 ^a	0.007 ^a	0.011 ^a	0.015 ^a

^a Six ears at 0° and 60° to rolling direction.

than at 90°. For 1200°F. final anneal, however, the majority of differences favor a slightly higher strength for 90° than for 0°. The variation in elongation for 0° and 90° only was apparently influenced by the penultimate anneal. For 800°F. penulti-

mate anneal and both 800° and 1200°F. final anneals, elongation at 0° is less than at 90°, while for 1200°F. penultimate anneal elongation at 0° is greater than at 90°. These observations indicate that the tensile strength-elongation relationship is

not a simple function, and elongation for a given strength is not necessarily constant.

Stress-strain curves, each of which is the average of three tests, are shown in Figs.

tests. The first part of the stress-strain curves, including the so-called elastic portion and that for the first plastic deformation up to 0.05 to 0.2 per cent strain,

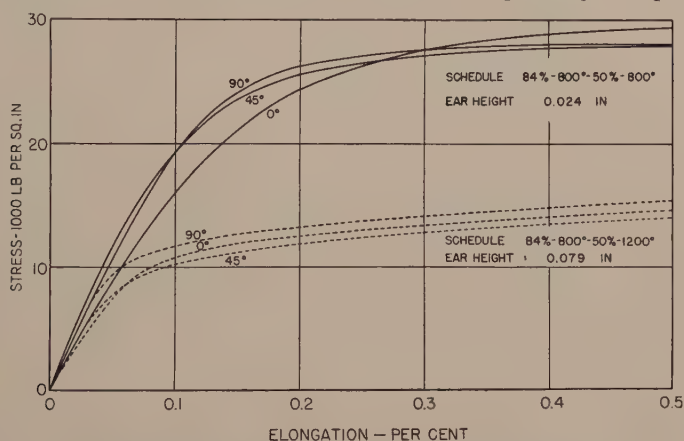


FIG. 5.—STRESS-STRAIN CURVES TO 0.5 PER CENT ELONGATION FOR TYPICAL MATERIALS SHOWING CONSIDERABLE VARIATION IN DIRECTIONAL PROPERTIES.

Each stress-strain curve is average of three tests. Test specimens cut at 0°, 45° and 90° to rolling direction.

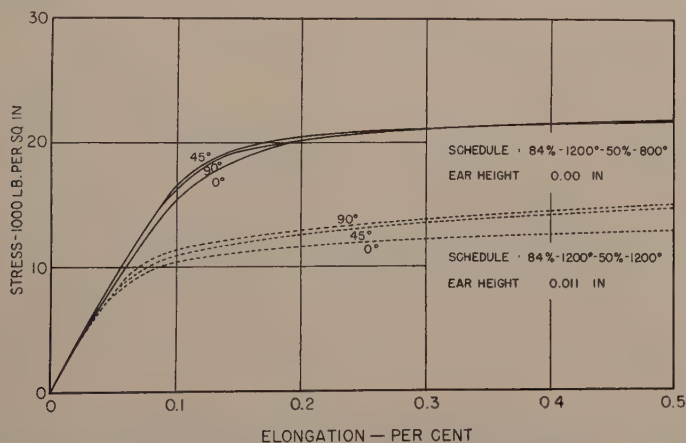


FIG. 6.—STRESS-STRAIN CURVES TO 0.5 PER CENT ELONGATION FOR TYPICAL MATERIALS SHOWING LITTLE VARIATION IN DIRECTIONAL PROPERTIES.

5-8 for materials with 84 per cent penultimate reduction, 50 per cent final reduction, and both 800° and 1200°F. penultimate and final anneals. These items showed various degrees of earing when cupped, ranging from no ears to extremely high ones. These stress-strain curves do reveal directional differences, but appear to give no more information than do the ordinary tensile

does not appear highly significant, other than disclosing an inconsistent directional variation in modulus of elasticity for the materials that produced eared cups. Some variation is to be expected as a result of preferred orientation. The inconsistency is probably due to the difficulty of accurately testing such thin material in this way. At 0.5 per cent, or shortly thereafter, the

curves are in the relation to each other that persists to fracture, and clearly show the directional effects.

The preferred orientation that must be

were constructed for specimens 153 and 175 (Figs. 9 and 10). While the preferred orientation was considerably more distinct for 153 than for 175, it was not very strong

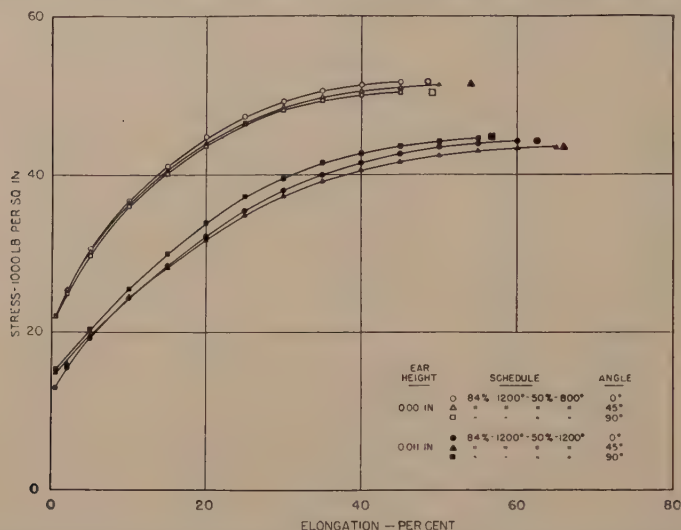


FIG. 7.—STRESS-STRAIN CURVES FOR MATERIALS OF FIG. 5 BEYOND 0.5 PER CENT ELONGATION. Larger symbols at right of curves indicate tensile strength and total elongation in 2 inches.

present is not so obvious in the microstructure of the brass as in copper, but does seem faintly evident in some of the tempers. The angular twin count used by Cook⁶ in his work with brass would probably reveal preferredness in many instances.

Six specimens were examined for preferred orientation, employing an X-ray diffraction method similar to that described by Barrett.¹⁰ Data concerning these samples are given in Table 3.

Complete pole figures showing the distribution of octahedral poles with regard to the rolling plane and rolling direction

in either case and only three degrees of intensity have been plotted. The solid triangles show the positions of (111) poles according to a symmetrical (110)[112] orientation. The comparable positions of poles corresponding to the usual annealing texture of brass (113)[112], or any other possible arrangement, are not shown because no other orientation was found to agree with the pole figure as well as that above.

Despite the fact that the pole figures for both specimens are rationalized by the same designation, the difference between

TABLE 3.—Preferred Orientation

Specimen No.	Penultimate Reduction, Per Cent	Penultimate Anneal, Deg. F.	Final Reduction, Per Cent	Final Anneal, Deg. F.	Final Grain Size, Mm.	Ears	
						Number	Height, In.
153	84	800	50	1200	0.090	4	0.079
175	50	1050	84	1200	0.100	6	0.015
24	84	1200	50	800	0.030	0	
40	37	1200	84	800	0.015	0	
169	37	800	84	1200	0.100	4	0.035
170	37	900	84	1200	0.090	6	0.018

the two is very distinct. The pole figure of specimen 153 (Fig. 9), representing material yielding four-eared cups, has four

specimen 175 (Fig. 10), representing material yielding six-eared cups, shows six areas of relatively denser (111) coverage

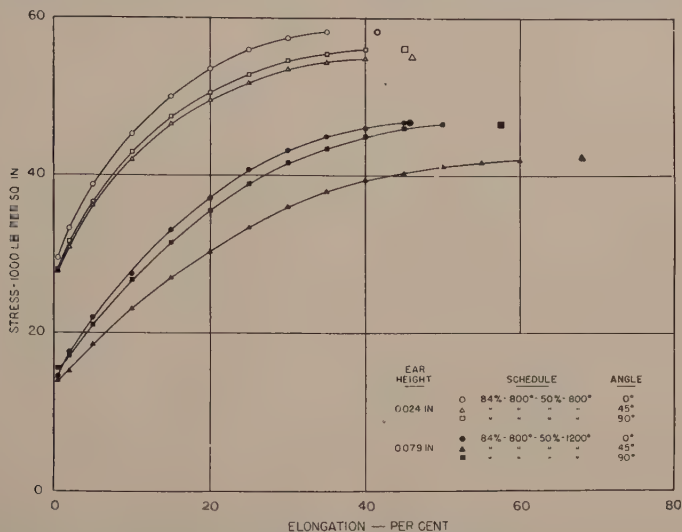


FIG. 8.—STRESS-STRAIN CURVES FOR MATERIALS OF FIG. 6 BEYOND 0.5 PER CENT ELONGATION.

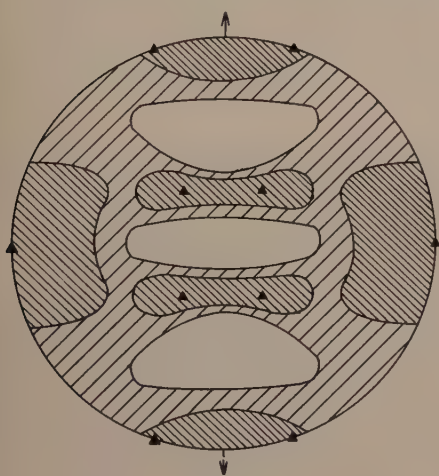


FIG. 9.

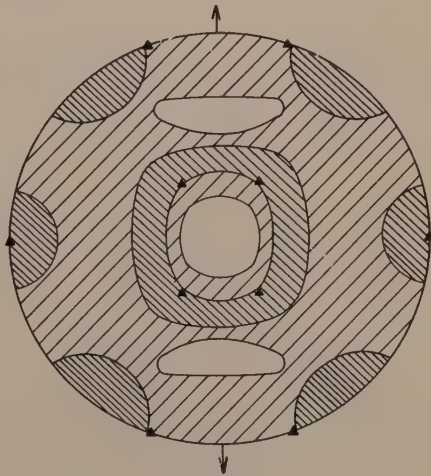


FIG. 10.

FIGS. 9 AND 10.—POLE FIGURES SHOWING DISTRIBUTION OF (111) POLES WITH RESPECT TO ROLLING PLANE AND ROLLING DIRECTION.

Fig. 8, material No. 153 (84 per cent 800°, 50 per cent 1200°). Cups made with this material had four ears, 0.079 inch high.

Fig. 10, material No. 175 (50 per cent 1050°, 85 per cent 1200°). Cups made with this material had six ears, 0.015 inch high.

areas of dense octahedral pole population around the periphery, at 0° and 90° to the rolling direction. The pole figure of

at 30° and 90° to the rolling direction. Both pole figures show three areas of lowest (111) population in similar positions.

There was less difference in intensity between the strong and intermediate shading around the periphery of the pole figure for specimen 175 than for specimen 153, corresponding to the lesser height of the ears for the former material.

It would seem unusual for these annealed brasses to show a texture better described by the usual rolling texture (110)[112] than by the recrystallization orientation (113)[112]. The latter texture, however, apparently has been found in brass subjected to extremely great reduction by rolling before annealing. It has already been shown⁸ that the empirical texture (113)[112] may in reality be the result of new grains in the deformation orientation and also twins therefrom. Although both of the present textures conform to the deformation orientation better than any other, there are distinct differences, which cannot be rationalized on the basis of the above theory.⁸ At present, the differences must be attributed to the presence of other complex orientations of unknown origin.

The X-ray diffraction patterns of the other specimens suggested the relative grain sizes and degree of preferred orientation and appeared to explain satisfactorily the degree of earing of cups drawn from each material.

SUMMARY

A study was made of the directional properties of annealed 68-32 brass strip as influenced by penultimate reductions of 37, 50 and 84 per cent; final reductions of 37, 50, 69 and 84 per cent, and penultimate and final anneals of 800°, 900°, 1050° and 1200°F., omitting the combinations that involved sequences of 84 per cent penultimate and 84 per cent final reductions.

Wide variation in directional properties due to the manner of processing was indicated both in cupping and in tensile tests. Ears on cups, when found, were

usually at 45° to the rolling direction, there being four ears per cup. There were, however, some cups with six moderate ears at 0° and 60° to the rolling direction. There were many conditions that produced no ears, and it was clearly indicated that preferredness or directionality caused by intermediate treatments could be reduced or eliminated by proper final treatments.

As a general conclusion, it can be stated that directionality or earing tendency increases with degree of both penultimate and final reductions, as penultimate annealing temperature decreases and as final annealing temperature increases.

X-ray analysis of typical materials was in satisfactory agreement with other tests. The recrystallization texture was found to be (110) [112] for the conditions that produced four-eared cups, and this was the only simple orientation applicable to the material that yielded six-eared cups, although the (111) poles were distributed differently in the two cases. In both cases the distribution of the (111) poles appeared to account for the earing encountered.

ACKNOWLEDGMENT

The authors wish to make due acknowledgment to Dr. D. K. Crampton for his interest in the investigation, to Dr. R. M. Brick for making the X-ray analyses, and to the Chase Brass and Copper Co. for permission to publish the results of the work.

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DISCUSSION

(L. S. Fletcher presiding)

ARTHUR PHILLIPS,* New Haven, Conn., AND
C. H. SAMANS,† Southbridge, Mass.—Some
years ago, in the course of our general study of

maximum of 69.86 per cent and a minimum of 69.52 per cent. Each bar analyzed also 0.01 per cent iron, less than 0.075 per cent lead, and the balance zinc.

This material was worked according to the 11 different schedules shown in Fig. 11. The metal

ROLLING SCHEDULES

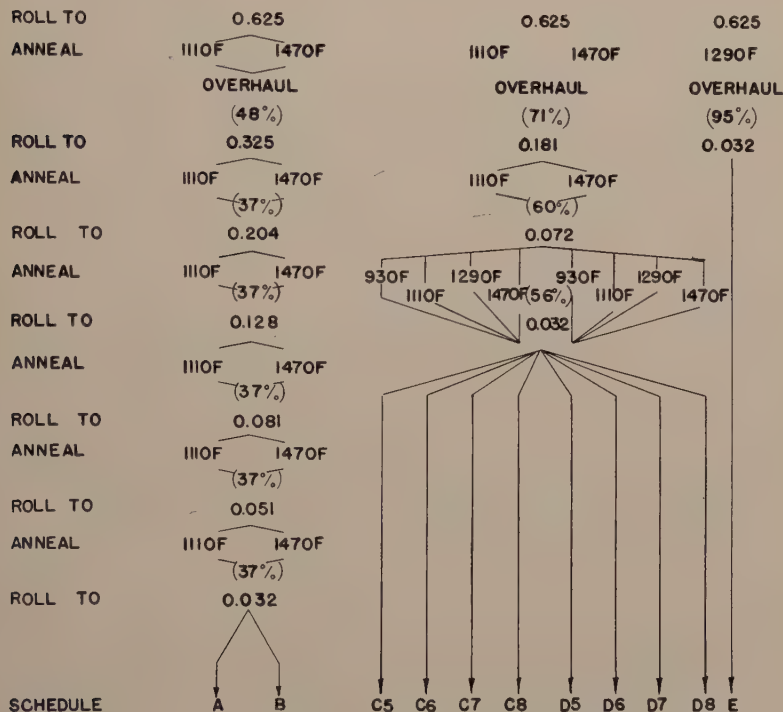


FIG. 11.—STEPS IN THE ELEVEN DIFFERENT ROLLING SCHEDULES USED TO PRODUCE 0.032-INCH GAUGE METAL.

directional properties at the Hammond Laboratory, a considerable amount of information on 70-30 brass was collected, which was never published because of the restricted financial budgets under which most of the technical societies were then forced to operate. The data we secured supplements and confirms so well the excellent work of the present authors that it seems desirable to present certain phases of it at this time.

Four bars of a commercial heat of 70-30 brass were used, varying in copper content between a

treated by schedules A and B was given identical reductions of about 37 per cent per pass, but different intermediate anneals. In schedule A, 1110°F. was used and in schedule B, 1470°F. The original work was planned for centigrade annealing temperatures, which accounts for the somewhat peculiar Fahrenheit values. The reductions in schedules C and D were somewhat greater, approximating 60 per cent per pass. In schedule C, 1110°F. was used for the intermediate anneals while 1470°F. was used for schedule D. In addition, for each of these two schedules, the penultimate anneal was varied: 930°, 1110°, 1290°, and 1470°F being used in

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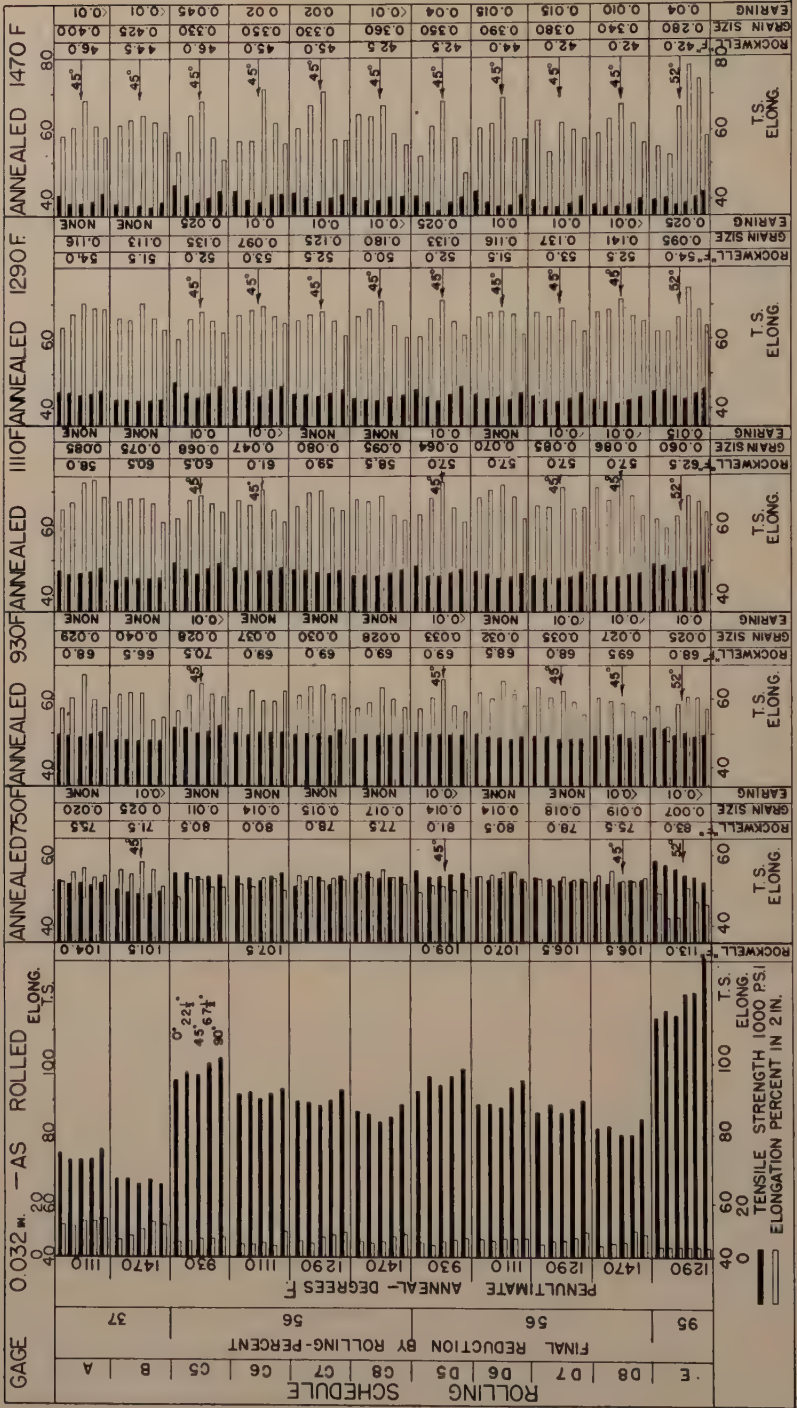


FIG. 12.—VARIATION OF PHYSICAL PROPERTIES WITH SPECIMEN ORIENTATION FOR ALL TREATMENTS STUDIED.

each case. Schedule E consisted of a very heavy reduction of 95 per cent without any intermediate anneal. All schedules finished on 0.032-in. gauge and final anneals of 30 min. at

presentation employed by the authors in their paper. In the hard-rolled materials, the directional effects are not manifested in the tensile properties to any marked extent except for the

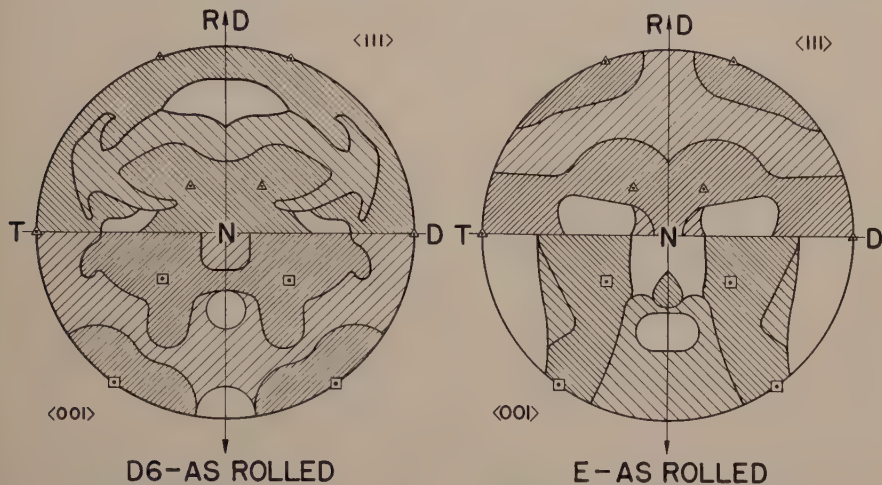


FIG. 13.—POLE FIGURES SHOWING THE ROLLING TEXTURES FOR METAL WORKED ACCORDING TO SCHEDULES D6 (1470°F., 60 PER CENT; 1110°F., 56 PER CENT) AND E (1290°F., 95 PER CENT).

750°, 930°, 1110°, 1290°, and 1470°F. were given to each of the lots of metal.

On both the hard-rolled and the annealed materials, Rockwell F hardness measurements were made and values for tensile strength and elongation were determined in triplicate at angles of 0°, 22½°, 45°, 67½° and 90° with the rolling direction. Metal rolled by schedule E was tested, in addition, at an angle of 52° with the rolling direction. X-ray pole-figure analyses were made of the rolling textures only for the metal rolled by the D6 and E schedules. In addition, grain-size measurements and six cupping tests were made on each of the lots of annealed metal, 330 cups in all. These cups were cut and drawn in one operation from a square piece, using a blank diameter of 2.058 in. and a die diameter of 1.120 in. The reduction of the cup wall was approximately 45.5 per cent. The cups were all drawn with the rolling direction of the original sheet in the same direction with respect to the press setup. The height of the ears on each of these cups was carefully determined, using a dial gauge, and the values so secured were averaged for each lot of six cups.

All of the physical test data are summarized in Fig. 12, using the same general method of

material given the 95 per cent reduction, schedule E. With schedules A, B, C and D, there is some tendency for the tensile strengths to be lower at 45° and higher at 90° and for the elongations to be higher in the 67.5° and 90° directions than in the specimens parallel to the rolling direction, but neither of these effects is pronounced. The differences in tensile strength seem to become more noticeable with increasing penultimate reductions and with decreasing penultimate annealing temperatures. In the metal rolled according to schedule E, there is a marked increase in the tensile strength as the angle between the test specimen and the rolling direction approaches 90°. The elongation, however, suffers little change.

As would be expected, for a given set of reductions the metal annealed at a lower penultimate temperature had a somewhat greater tensile strength and hardness than that annealed at a higher temperature.

The pole figures (Fig. 13) showing the <111> and <100> textures for the hard metal rolled according to schedules D6 and E are included more because of their possible value to any future workers in this field than because of their utility in assisting the interpretation of the present data. The relation,

ship between pole figures and physical testing data is as yet not too clearly understood, as the authors have pointed out. Both pole figures can be explained by the usual $\langle 110 \rangle - [112]$

materials that had been given very heavy reductions of the order of 95 per cent would tend to give ears at 52° to the rolling direction. Somewhere between these two ranges, there

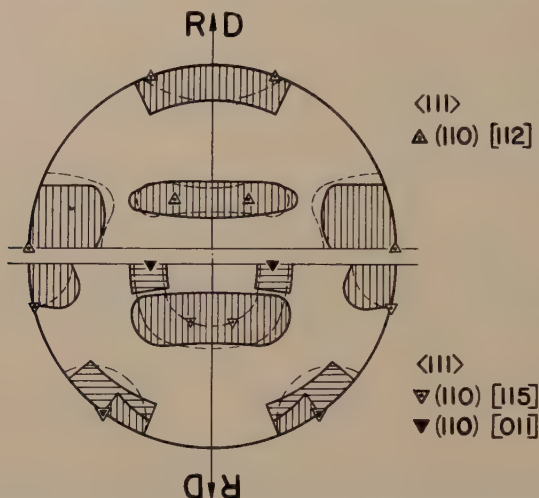


FIG. 14.—RATIONALIZATION OF RECRYSTALLIZATION TEXTURES FOR AUTHOR'S TREATMENT NO. 153 (FOUR EARS) AND NO. 175 (SIX EARS).

Top, compare Fig. 9; bottom, compare Fig. 10.

rolling texture although there are certain noticeable differences between them. They agree well with the data of Brick.

The grain-size measurements on the annealed materials agree, in general, with the observations made by the authors, although there are one or two minor differences. The Rockwell hardness values also are in good agreement with the average grain diameters, tending to decrease as the grain size increases.

Most of the cups showing earing had four ears at 45° to the rolling direction just as observed by the authors. All of the annealed materials that had been rolled according to schedule E, however, had four ears at 52° rather than at 45° to the rolling direction. This material was given a somewhat greater reduction than that found by the authors to give six ears at 60° to each other.

This suggests possibly the occurrence of at least two main preferred orientations in the recrystallized material. One of them, found in some annealed materials after low and intermediate reductions up to at least 60 per cent, would tend to give ears at 45° to the rolling direction. The second found in annealed

might then be expected a region of overlap in which a double orientation would exist, and which would tend to give three sets of ears at 60° to each other, as found by the authors in the material rolled 84 per cent. It might be pointed out that the pole figures found by the authors could also be rationalized very well in this manner as indicated in Fig. 14. In the upper half, the texture of their Fig. 9 has been idealized as a distribution in which a $\langle 110 \rangle$ plane lies in the rolling plane and a $[112]$ direction in the rolling direction with a 20° deviation of the rolling direction toward $[111]$ and a 5° deviation toward $[115]$, and with a rotation about the rolling direction of $\pm 25^\circ$, and a rotation about the transverse direction of $\pm 12^\circ$. In the lower half the texture of Fig. 10 has been idealized as a combination of two distributions in which a $\langle 110 \rangle$ plane lies in the rolling plane and: (a) a $[115]$ direction lies in the rolling direction with a 15° deviation toward $[112]$, and with a rotation of $\pm 15^\circ$ about the rolling and the transverse directions; (b) a $[110]$ direction lies in the rolling direction with a deviation of $\pm 15^\circ$, and with a rotation of $\pm 10^\circ$ about the

rolling direction and $\pm 15^\circ$ about the transverse direction.

Unfortunately, at the time our data were secured, equipment was not available for securing pole-figure data on recrystallized material, so we can offer no information that might serve to indicate whether or not this hypothesis would be verified by the texture of the annealed metal rolled according to schedule E.

The tensile data and the cupping data on our materials agree well with the results found by the authors. The two conditions found to be most favorable for earing were: first, heavy final reductions and high final annealing temperatures; and second, intermediate final and penultimate reductions and low penultimate anneals, with a final annealing temperature greater than the penultimate annealing temperature, regardless of what the annealing temperatures were before the penultimate stage. Likewise, the conditions least favorable for earing were: first, light final and penultimate reductions regardless of the final annealing temperature; second, final annealing temperatures lower than those used for the penultimate anneal regardless of the final reduction.

As noted by the authors, when earing occurred the maximum tensile strength was usually found at 0° and 90° to the rolling direction and the maximum elongation invariably was found to coincide closely with the direction of maximum earing.

We feel that the tremendous amount of effort the authors have put into securing the data shown in their paper has made a worthy contribution to the field of directional properties, even though they have found, as have several before them, that a strictly quantitative relationship between physical properties, preferred orientations, and earing tendencies is difficult to secure. It is hoped that the supplementary data we are able to furnish from our own work will add to the value of the authors' data and ultimately will be of some assistance to the workers who succeed in uncovering the exact relationships involved. The solution of this problem is a complex one and when it is finally secured, reliable data, such as those so carefully obtained and so well presented by the authors, will be of great value in verifying it.

The practical importance of this subject is realized by any maker of brass or brass products who has ever had to contend with earing in his manufacturing operations. It would seem that the data collected by the authors would enable the almost complete elimination of these troublesome phenomena. It might be interesting to know, however, whether treatments similar to those they have found to be suitable would prevent the development of ears in operations involving several redraws. Possibly the authors have some information on this point?

H. P. GEORGE,* J. B. REED,* AND F. SEITZ,†
Philadelphia, Pa.—The authors of this paper are to be congratulated on their timely contribution to the knowledge of recrystallized structures occurring in brass subjected to commercial reductions. The majority of previous investigations have dealt with material subjected to higher reductions than usually are encountered commercially. While such investigations are of value in showing what can occur under extreme conditions, any knowledge of directional properties is of limited practical value unless it is known to apply in commercial practice.

Frankford Arsenal is interested in this subject because of cartridge assembly difficulties which are encountered when ears are developed on primer cups as a result of a preferred orientation of the primer strip. It appears from an X-ray investigation and an angular twin count that quite a low degree of preferred orientation is sufficient to produce objectionable ears. While no attempt was made to obtain a complete pole figure, the results on commercial strip that produced four ears on drawing were consistent with a (110) [112] type of orientation.

With regard to paragraph 1 on page 154, it is not quite clear to us what the authors mean when they say "The preferred orientation that must be present is not so obvious in the microstructure of the brass as in copper, but does seem fairly evident in some of the tempers." It is assumed that they refer to a visual estimation of preferred directionality of twin bands. Is this assumption correct?

* Frankford Arsenal.

† University of Pennsylvania.

We should also like to ask if an attempt has been made to identify the recrystallization texture shown in Fig. 10 with one of the orientations, such as (110) [113] found by Brick⁸ in the deformation of single crystals of brass.

G. EDMUNDS,* Palmerton, Pa.—I wonder if Dr. Burghoff and Dr. Bohlen have studied pole figures of the metals that did not produce ears. I asked that because any raw material may be expected to exhibit directional properties and yet these are not always associated with earing.

Perhaps the intensity of the various orientations rather than the type of orientation pattern may be the deciding factor.

I should also like to know how far the authors feel they could go in predicting directional properties—that is, including tensile strength, tensile elongation, and earing—on the basis of pole figures.

R. M. BRICK,† New Haven, Conn.—The pole figure (Fig. 9) shows strong concentrations of poles of octahedral planes near the periphery and at 0 and 90° to the rolling direction. These poles are the ones of significance in regard to flow characteristics of the metal. They show that there is a tendency for octahedral planes to occupy positions normal to the surface of the annealed sheet and at 0 and 90° to the rolling direction. If a test specimen is cut from this sheet with its axis in the rolling plane and at either 0 or 90° to the rolling direction, there is no appreciable number of slip planes in the preferred position for flow; that is, at 45° to the flow direction. If the test specimen is cut with its axis in the rolling plane and at 45° to the rolling direction, there is a concentration of slip planes in a position of maximum resolved stress, facilitating flow; i.e., at 45° (in reality, from about 35° to 55°) from the axis of stressing. Consequently, this pole figure would predict most ready flow, and thus ears, at positions *between* the areas of maximum octahedral pole concentration around the periphery of the figure. This analysis is not, of course, new but is worth mentioning in view of questions as to the usefulness of pole figures. The predictions necessarily are qualitative, although the method should differentiate between different degrees of earing if the differences are very large.

* New Jersey Zinc Co.

† Hammond Laboratory, Yale University.

H. E. STAUSS,* Newark, N. J.—In the platinum industry, we are not bothered much by earing as such, but we do have a number of problems that indicate directionality in the materials. We deal with rather small quantities and in general our solution of the problem of directionality lies in producing grains small in comparison with the metal specimen. In other words, we try to achieve isotropic plasticity by making the nonisotropic units, the crystals, as small as possible with respect to specimen size.

Is it correct that in the case of earing we are facing a problem relating only to structure or to grain size? Some of the data are suggestive that there may have been incomplete removal of strains. We find that strains must be removed as well as the grain size restricted, otherwise ability to fabricate the metal is restricted.

H. L. BURGHOFF (author's reply).—The discussion presented by Messrs. Phillips and Samans constitutes in itself a very considerable fund of information upon directional properties and earing of cups of brass. Dr. Samans' analysis of Fig. 10, the pole figure for material that yielded cups with six ears, is an interesting contribution. It appears to make the situation more satisfactory than that in which the authors were obliged to leave it.

No instances of ears developed in redraw operations have come to the attention of the authors. This may be due to the fact that, for most economical processing, the metal is annealed after rather moderate working. Articles such as socket shells, which are severely worked in cupping and drawing operations, usually are processed to their final dimensions without intermediate anneals. The study of the development of preferred orientations in tubular articles is complicated by the type of working; i.e., the relative reductions of both diameter and wall thickness, as well as by the degree of working between anneals.

Messrs. George, Reed and Seitz are correct in assuming that indication of preferred orientation in the microstructure is given by preferred directionality of twin bands. As Palmer and Smith point out in their paper, such preferredness is most evident on longitudinal sections normal to the rolled surface.

The explanation offered by Dr. Samans

* Physics Department, Baker and Co.

appears to be the most rational solution of Fig. 10. Although somewhat similar textures have been reported in Dr. Brick's works^{8,9} they cannot be explained by a single orientation.

With regard to Mr. Edmunds' questions, no attempt was made to set up pole figures for materials that did not produce ears. X-ray diffraction patterns of such materials indicated entirely random orientations. The use of pole figures in predicting directional properties is only qualitative, of course, although differences in degree of preferredness may be indicated by the X-ray diffraction patterns. Dr. Brick's discussion is of interest in this connection.

Mr. Stauss suggested that the problem of directional characteristics might be one of

grain size only. While it is true that the most severe earing occurs in metal of large grain size, it is also true that earing of large-grained metal can be avoided. The directional properties of the metal are associated with the anisotropic nature of the individual grains and hence with the manner of their orientation in the aggregate. Isotropic properties are attained in a state of random orientation.

The thought was also advanced that strains in the metal may have been incompletely removed in some cases. However, all of the annealed material that was tested was found by microscopic examination to be completely recrystallized and free of any strained areas from the previous cold-working.

Effect of Some Mill Variables on the Earing of Brass in Deep Drawing

BY EARL W. PALMER* AND CYRIL STANLEY SMITH,* MEMBERS A.I.M.E.

(New York Meeting, February 1942)

STRIP of any of the metals used for deep drawing operations occasionally yields cups that are defective because of a rim that varies in height around the cup in a wave-like manner. Some such defects are traceable to tools or other press factors, but when the protuberances formed (usually four in number on brass and other copper alloys) are symmetrically disposed with respect to the rolling direction of the strip, they are invariably attributable to the metal. The effect is known as "earring" and the protuberances are called "ears." Other terms frequently heard are "tips," "scalops," and "corners." It is recognized that the effect is most commonly a result of a directional crystal structure produced by rolling and annealing operations in the manufacture of the metal strip. Numerous papers dealing with various aspects of the earing effect have appeared in the literature, those listed in the references¹ being especially interesting and valuable.

An investigation of the factors influencing earing of brass cups has been in progress in the laboratories of the American Brass Co. for several years, and it was thought desirable to make some of the results generally available in summarized form. The present paper discusses many factors that do and do not contribute to ear formation. In addition, a section is devoted to

methods of minimizing the earing tendency of brass sheet by proper selection of the cold-rolling and annealing schedule by which it is produced.

In the space available, it is impossible to quote detailed experimental procedures and numerical results. However, the authors make no statement that they do not believe to be properly substantiated, either by experimental evidence obtained under laboratory conditions or by experience in the actual production of deep-drawing brass in the brass mill.

MECHANISM OF EAR FORMATION

It must be clearly understood that the formation on cups of symmetrical ears, four or more in number, is attributable solely to the strip metal, and results from the strip having different deformation characteristics in different directions. The tools used in the drawing process, or the type and completeness of lubrication of the strip, have nothing to do with the problem of ears, although they do, of course, greatly affect the "drawing quality" of the strip and the general appearance of the cup. A single tip may be drawn up on the rim of a cup because of misalignment of the tools, or because the gauge of metal varies from side to side of the strip. The two-ear form that sometimes appears is also traceable to gauge variations. However, the four-ear and six-ear symmetrical forms that we are concerned with here are caused by factors inherent in the structure of the metal itself.

Manuscript received at the office of the Institute Nov. 5, 1941. Issued as T.P. 1444 in METALS TECHNOLOGY, June 1942.

* Assistant Research Metallurgist and Research Metallurgist, respectively, American Brass Co., Waterbury, Conn.

¹ References at end of paper.

Fig. 1 shows stages in the cupping of a normal nonaging material, as compared with the behavior of a strip that yields a cup with four well developed ears. The

certain definite directions on certain definite planes in the crystalline metal grains. In normal polycrystalline brass the individual crystalline grains are oriented at

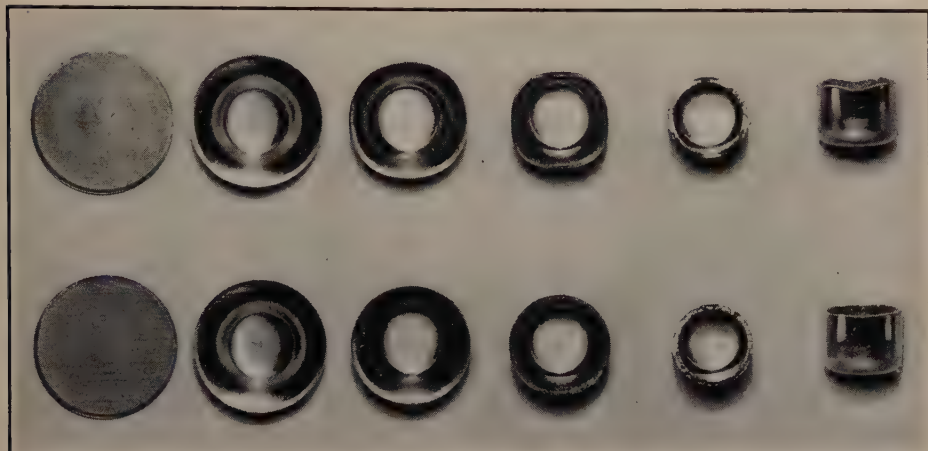


FIG. 1.—STAGES IN FORMATION OF CUPS FROM STRIPS THAT DO AND DO NOT FORM EARS. Cups 0.540-in. diameter from blanks 0.940-in. diameter; 0.040 in. thick.



FIG. 2.—PROFILES OF CUPS, SHOWING TYPES OF EAR FORMATION.

a, six-ear forms; *b*, four-ear forms. Height of ear magnified about five times with respect to circumference. Angles from rolling direction indicated.

different kinds of ear formation that have been observed are typified in the cup profiles of Fig. 2.

It is now common knowledge that deformation of metals takes place by slip in

random, so that approximately equal numbers of planes of easy slip are available for deformation in any direction. In cupping such material, the blank will draw in uniformly all around its circumference and

no ears will appear. However, if for any reason the crystal orientations of the individual grains of a strip become aligned, the strip as a whole will behave more or less like

sively fragmented, and the crystalline fragments rotated by the process, so that all tend to align themselves in definite relation to the direction of rolling. For a given

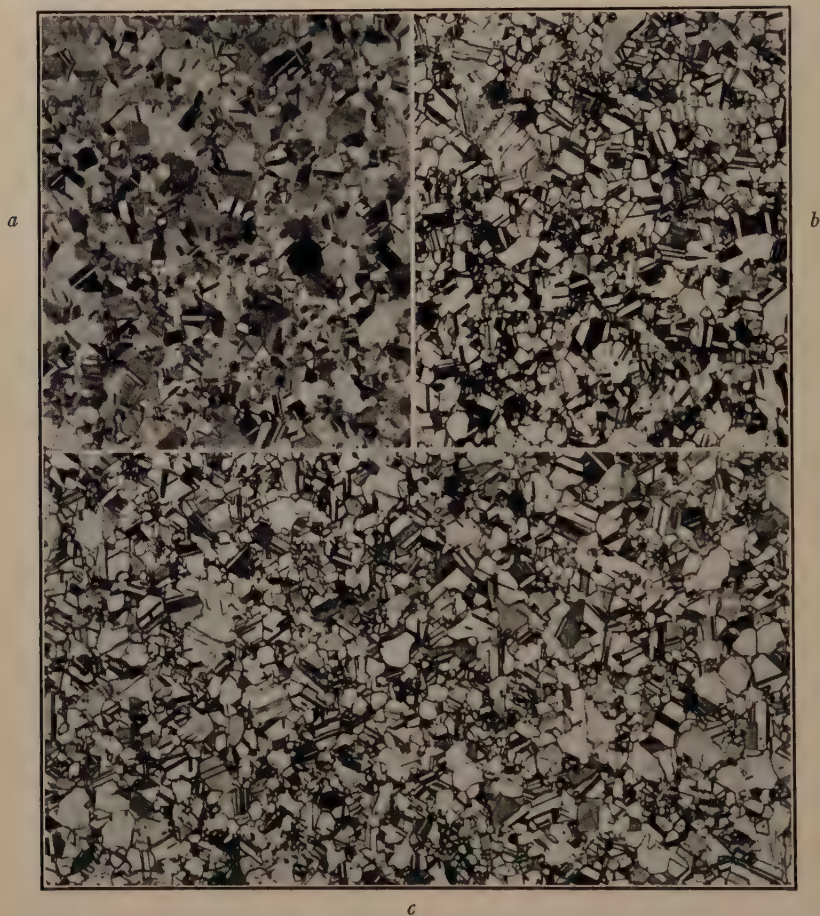


FIG. 3.—MICROSTRUCTURE OF HIGHLY DIRECTIONAL 70-30 BRASS STRIP. $\times 75$.
Etched in ammonia plus hydrogen peroxide.
a. Section parallel to surface. Rolling direction horizontal.
b. Cross section. Surface horizontal.
c. Lengthwise section. Surface horizontal.

a single crystal, and its deformation characteristics will vary with direction. In a cupping operation such material will produce ears, of a height that depends upon the perfection of the grain alignment.

Under unidirectional deformation, as in normal rolling practice, the individual grains of an annealed material are progres-

sively fragmented, and the crystalline fragments rotated by the process, so that all tend to align themselves in definite relation to the direction of rolling. For a given grain size the degree of alignment, or directionality, depends almost entirely upon the amount of deformation, unless the annealed material is already directional as a result of previous treatment. Whatever the extent of structural alignment in a rolled strip, it is in some degree preserved after annealing. The precise orientation of the new crystals

in the annealed material usually differs from that of the fragments in the rolled material, although the two are closely related.

could be wished, largely because of experimental difficulties in covering a sufficient area of specimen and in avoiding variable absorption effects at the important posi-

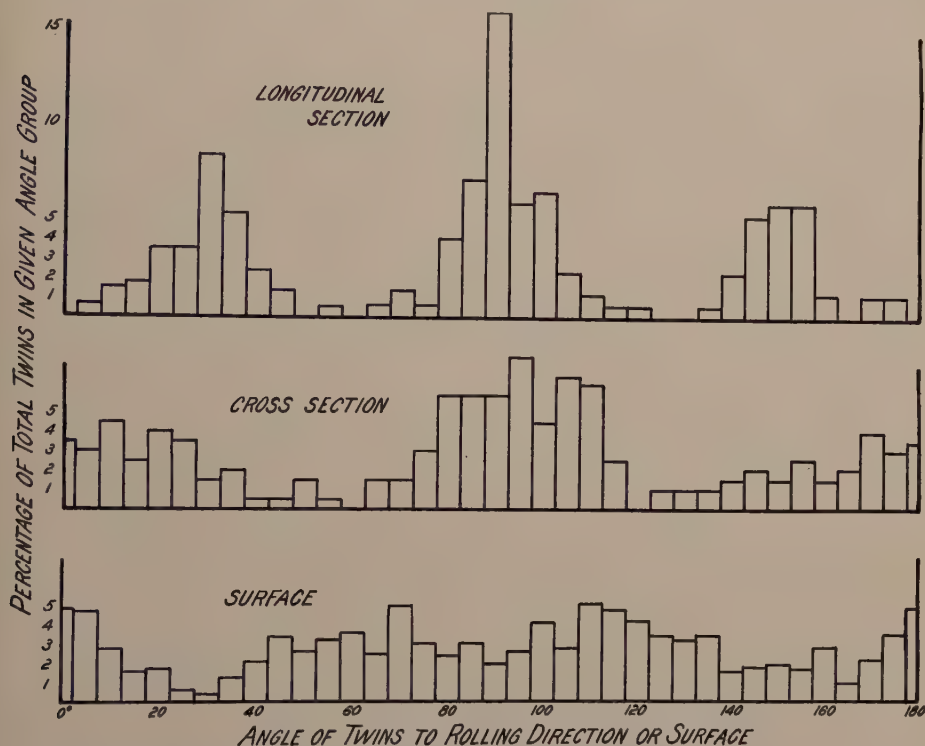


FIG. 4.—TWIN FREQUENCY CURVES.

Surface, longitudinal and cross sections of 65-35 brass strip rolled 24 B. and S. numbers, from a grain size of 0.120 mm., and annealed at 750°C.

Detection of Directionality in Annealed Brass

Grain alignment of brass strip may be demonstrated in a number of ways. The most basic approach to the problem is by means of pole figures derived from X-ray diffraction photographs. If properly made these indicate the distribution of the crystallographic slip systems in all directions of the strip and hence ideally could permit quantitative prediction of deformation characteristics. Unfortunately, some of the published work of this kind dealing with copper-zinc alloys is not as satisfactory as

tions where the specimen is at a small angle to the X-ray beam.

In extreme cases directionality becomes readily apparent under the microscope as an obvious alignment of twin bands in certain preferred directions, and as a change from the normal distribution of grains etching in all degrees of contrast from black to white, to one in which there is a preponderance or an absence of certain shades. The alignment of the twins is least apparent on the surface of the strip and shows most clearly on a longitudinal section normal to the surface. This is illustrated in Fig. 3, which includes photomicrographs of longi-

tudinal, transverse, and surface sections of highly directional annealed 0.033 in. gauge cartridge-brass strip.

be used to indicate the degree of twin alignment. This is illustrated in the three curves of Fig. 4, showing twin-direction frequency

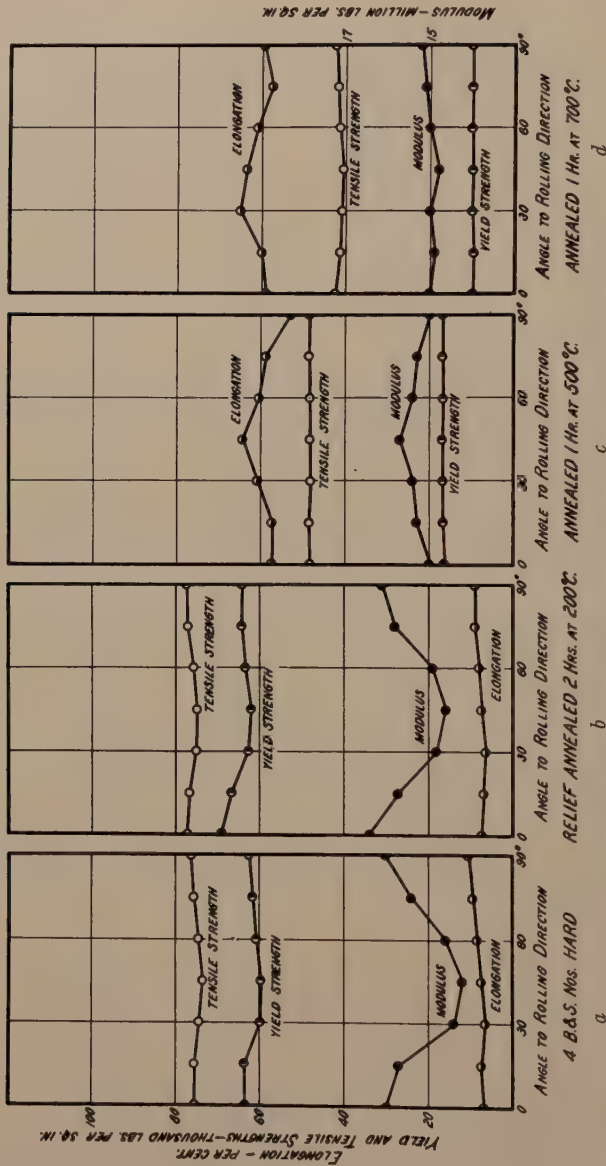


FIG. 5.—DIRECTIONAL VARIATION OF TENSILE PROPERTIES IN 65-35 BRASS STRIP. Material 0.020 in. thick, processed with normal reductions (4 to 6 B. and S. numbers) and normal anneals (about 600°C.). Final treatments: (a) rolled 4 B. and S. numbers hard; (b) relief anneal 2 hr. at 200°C.; (c) annealed at 500°C. (0.038 mm. grain size, no ears); and (d) annealed at 700°C. (0.120 mm. grain size, no ears).

A distribution curve, showing the percentages of the total number of twins present that make given angles with the rolling direction or other reference line, may

for the surface, cross section, and lengthwise section of a 65-35 brass rolled from 0.430 to 0.028 in. (24 B. and S. numbers) and annealed 1 hr. at 750°C. The peaks

when analyzed on a stereographic projection on the assumption that the twinning plane is the (111) show that the most frequent orientation is with the (110) plane

earing behavior in Figs. 5 and 6. In the strip shown in Fig. 7 directionality is indubitably present and shows in the modulus variation, though it is of such a

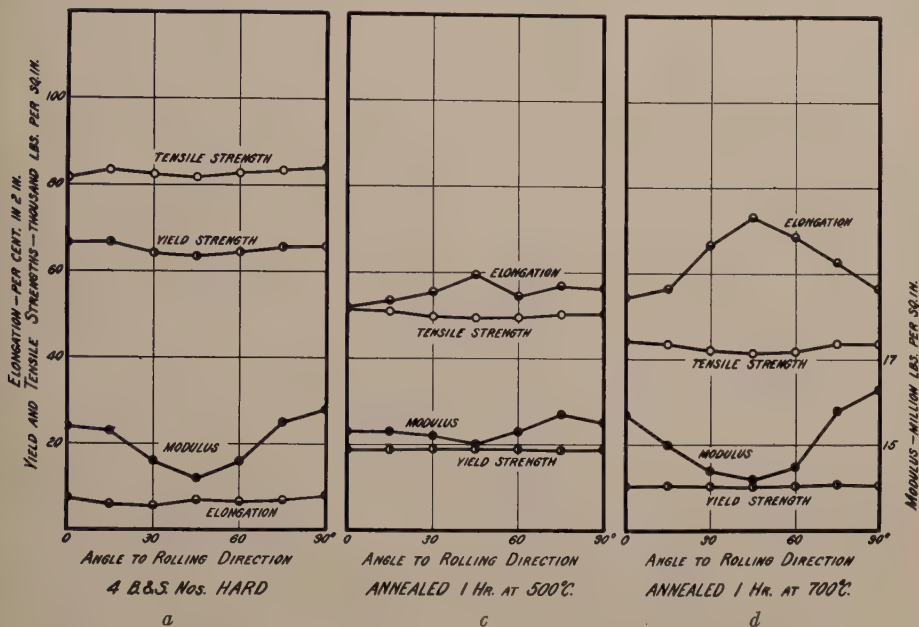


FIG. 6.—DIRECTIONAL VARIATION OF TENSILE PROPERTIES IN 65-35 BRASS STRIP.

Material 0.020 in. thick processed with normal reductions (4 to 6 B. and S. numbers) but low-temperature processing anneals (about 425°C.). Final treatments (a) rolled 4 B. and S. numbers hard; (c) annealed at 500°C. (0.030-mm. grain size, 0.010-in. ears on a 0.500-in. dia. cup); and (d) annealed at 700°C. (0.120-mm. grain size, 0.032-in. ears on a 0.500-in. dia. cup).

in the surface and the [112] direction in the rolling direction. Curves of this type must, however, be interpreted with caution, since not every grain in a section is visibly twinned and the number of twins in a given direction is a figure not necessarily related to the volume of metal in that orientation.

Directionality may also be detected by tensile tests of specimens cut in various directions of the strip. The variation of tensile properties with angle to the rolling direction of a number of samples of 65-35 brass, after various treatments, is shown in Figs. 5 to 7. The variation of elongation with direction is closely related to the earing behavior of the metal. The modulus of elasticity is a basic index of crystalline directionality and its variation follows

character that it does not produce appreciable earing for the lower temperature of final anneal. Modulus determinations of suitable accuracy on thin strip are extremely difficult and are not suitable for routine determinations of directionality.

While earing is usually traceable to the alignment of grains in annealed strip, other causes are occasionally found. Material finished with a light cold reduction (sometimes done to improve gauge or surface) may show slight ears when cupped. Partially recrystallized material behaves similarly. Finally, strip metal in which appreciable coring persists, or which contains streaks of beta or other constituent, may develop ears as a result of its mechanical fiber.

FACTORS WITHOUT EFFECT ON DIRECTIONALITY

Before discussing the factors that do have some bearing on the development of earing tendency, it seems desirable to dispose of some that are popularly, but erroneously, supposed to be of importance.

Rolling Mills and Technique.—The type or speed of rolling mill on which the metal is reduced has an insignificant effect on the development of directionality. Our studies have included two-high rolls of both 5-in. and 18-in. diameter, and four-high mills with work rolls of both 6 and 14½-in. diameter. Material reduced on the Steckel mill is practically indistinguishable in structure and behavior from that rolled to the same degree on four-high rolls.

So, too, the number of passes used (or the reduction per pass) is unimportant as far as earing is concerned. Ears virtually identical in height and shape were formed on cups made from strip rolled from 0.400 to 0.02 in. and annealed, regardless of whether this reduction was accomplished in thirty passes or in four. This was shown for brasses with 5, 31 and 35 per cent zinc.

No effect on earing behavior has been detected that could be attributed to difference in lubrication of the strip in rolling. There is a possibility that this factor, as well as roll diameter and reduction per pass, might become important with strip of thickness below about 0.009 inch.

It makes no difference whether the strip is rolled always in the same direction, or turned end for end between passes. Cross rolling does affect directionality but since this operation is not commercially feasible with strip metal it need not be discussed here.

Surface Finish of Strip.—The surface finish of the strip has been varied over a wide range without appreciable effect on the earing behavior. Cups show the same size and shape of ears whether made from black strip, or from strip pickled in sul-

phuric acid or red dip; whether bright dipped, or given a deep roughening etch. Lubrication in cupping also was without effect on ear formation, though it does, like the condition of the surface, greatly affect tool wear and the maximum draw possible in a given metal.

Impurities.—Lead and iron, the common impurities in copper-zinc alloys, have no appreciable effect on earing tendency when present in the usual amounts of about 0.02 per cent each. Lead may be present in considerable excess of this (as high as 0.5 per cent has no effect), but iron above perhaps 0.05 to 0.10 per cent causes characteristic multiple twinning of the grains and restriction of grain growth, which affect directionality in a complex fashion.

Silicon (0.1 per cent), manganese (1 per cent), nickel (1 per cent), aluminum (1 per cent), and cadmium (0.5 per cent) were found to be without significant effect on the earing of brasses adjusted in zinc content to be equivalent to a 65-35 alloy in structure, and probably can be tolerated in larger amounts. Very small amounts of lithium and sodium, such as might be added for deoxidation purposes, were also found to be without appreciable effect.

Casting Directionality.—The size and orientation of grains in the casting is not a significant factor in the development of directionality, for their effects are quickly removed and completely obscured by the subsequent normal cycles of cold-rolling and annealing.

FACTORS THAT AFFECT DIRECTIONALITY

The most important factors affecting directionality are the amounts of reduction given to the metal between anneals (especially at the final and ready-to-finish stages) and the temperatures of the various anneals. These two factors are interrelated in a complex fashion, and the discussion of one necessarily involves repeated reference to the other. However, an attempt will be made to separate these factors as much as

possible, and to consider them as separate stages in a production schedule. Less important factors having a bearing on directionality are discussed first, in order that the limitations of the data available

height. Such changes as do occur are probably largely a result of the fact that the larger punch radius used with the heavier gauges permits displacement of relatively more metal from the bottom of the cup.

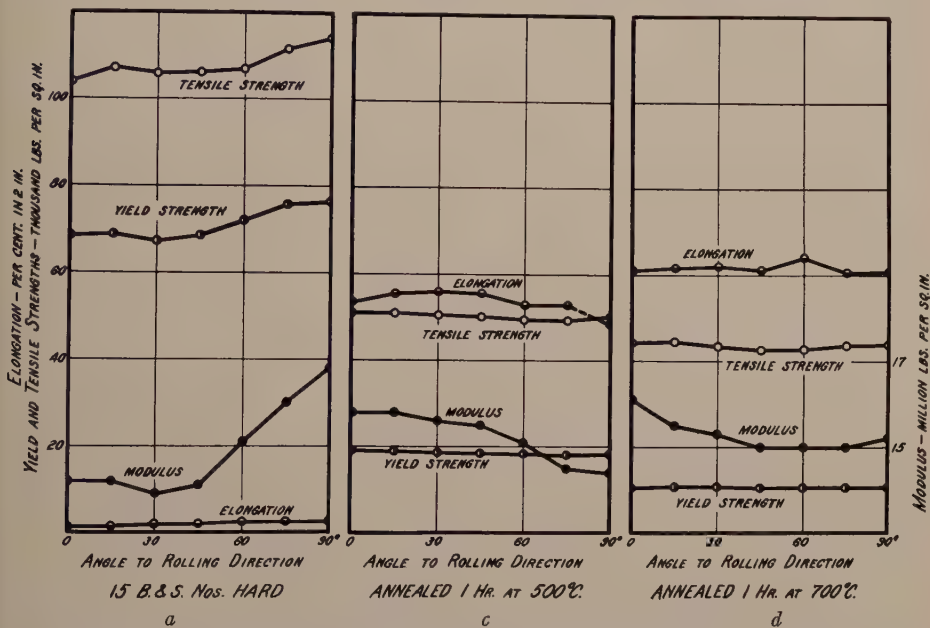


FIG. 7.—DIRECTIONAL VARIATION OF TENSILE PROPERTIES IN 65-35 BRASS STRIP.

Material 0.020 in. thick processed with two heavy balanced reductions. Annealed at about 700°C. at 0.430 in., rolled to 0.128 in., annealed at about 700°C., rolled to 0.020 in. Final treatments (a) 15 B. and S. numbers hard; (c) annealed at 500°C. (0.030-mm. grain size, no ears), and (d) annealed at 700°C. (0.115-mm. grain size, 0.021-in. ears on a 0.500-in. dia. cup).

on the two major factors may be clearly understood.

Gauge of Strip and Size of Cup.—These factors influence the height of ears formed to an extent that seems to depend solely upon obvious geometrical considerations. The actual ear height on cups made from metal of equivalent directionality will increase with increasing height of the cup wall, but expressed as a percentage of that height will be roughly constant, regardless of whether the difference in height results from increased diameter reduction or increased ironing. For cups of the same diameter and height, made from metal of equivalent directionality, a fairly wide variation in gauge has little effect on ear

Composition of Alloy.—It may be said that, in general, directionality in alpha copper-zinc alloys is more readily developed the higher the zinc content, especially with directionalities arising from high final reductions. Ears on copper cups usually, but not always, occur at 0° and 90° to the rolling direction. This behavior is different from that of the commercial copper-zinc alloys, for even those containing as little as 5 per cent zinc commonly form ears at 45° to the rolling direction. As far as we know at present, with pure alloys, a complex structure resulting in six ears instead of four occurs only in the brasses of higher zinc content. This form seems to consist of the usual 45° ears, shifted slightly,

with an extra pair of ears in the rolling direction.

As stated before, there are many impurities that have no significant effect on earing

sizes remain the same. Supposedly they would have the same effect in copper-zinc alloys of any composition, for phosphorus, at least, has been found to behave similarly

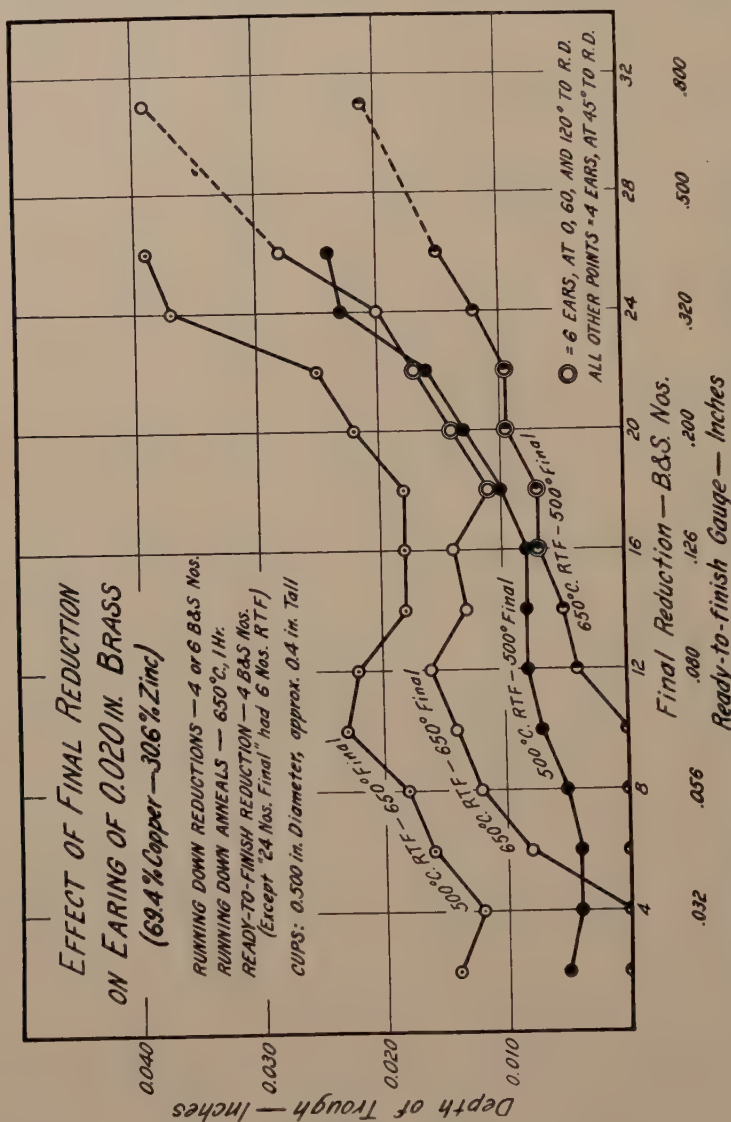


FIG. 8.—EFFECT OF [AMOUNT] OF FINAL REDUCTION ON THE EARING OF 0.020-IN. 70-30 BRASS STRIP. Material at ready-to-finish anneal was substantially nondirectional in all cases.

characteristics, but both phosphorus and arsenic in amounts of 0.05 to 0.10 per cent have been found to reduce ear height on 65-35 brass by as much as 50 per cent under optimum conditions, even when all grain

in 65-5 gilding metal. In the absence of iron phosphorus has no effect on the grain size of 65-35 brass after a given anneal. In the presence of more than 0.01 per cent iron, however, phosphorus materially restricts

grain growth, and this also modifies the earing behavior.

Amount of Reduction between Anneals.—The complex nature of the development of directionality by cold-rolling is apparent from Fig. 8, which shows the average depth of the trough* between adjacent ears on a cup as a function of the final reduction in B. and S. numbers.† The material was brass containing 31 per cent zinc, but the behavior is characteristic also of common high brass.‡ Curves are shown for ready-to-

* "Depth of trough" appears to be the most satisfactory measure of earing tendency. The troughs between the ears are frequently irregular but their tops usually lie in a single plane, which forms a convenient base for measurement. Troughs at 0° and 180° to the rolling direction are often less deep than those at 90°. Commercially, the deepest trough alone is important, since it determines trimming scrap.

† In depicting the effects of cold-work, the use of a logarithmic scale of reduction is greatly to be preferred to a linear per cent reduction scale, since with the former successive reductions are continuously referred to the new gauge rather than to the original thickness of the piece. Any logarithmic scale could be used, but the B. and S. gauge is convenient and is already extensively used in the brass industry. The numbers are based on the Brown and Sharpe thickness or diameter gauge numbers, but in considering reductions are used as ratios regardless of actual thickness. The thicknesses follow a geometric progression, the thickness at each whole number being 0.89054 of the preceding one. Alternately $\frac{T_0}{T} = (1.12293)^x$, where

T_0 and T are the initial and final thicknesses, x is the B. and S. numbers reduction and 1.12293 is the arbitrary constant of the B. and S. scale. The 6th power of 1.12293 is 2.0050, hence 6 B. and S. numbers reduction are closely equivalent to 50 per cent reduction in thickness.

The common slide rule is convenient for making these computations. The equation can be rewritten: $\log T = \log T_0 - x \cdot \log (1.12293)$. The latter logarithm is 0.0503, close enough to $\frac{1}{20}$ to permit the linear L scale of a slide rule to represent 20 B. and S. numbers against actual thicknesses on the D logarithmic scale, or 40 B. and S. numbers on the A scale. The factors of 20 or 40 are easily applied mentally, permitting direct reading of B. and S. numbers for any reduction that may be encountered.

‡ The cups measured for the data in Fig. 8 were 0.5-in. diameter and about 0.4 in. tall, made from 0.94-in. diameter blanks of 0.020-in.

finish anneals at both 500° and 650°C., and final anneals at these same two temperatures. Pre-ready-to-finish treatment was such as to render the material substantially nondirectional at each of the various gauges required at this stage.

With the 650°C. ready-to-finish and final anneals, the earing behavior passes through five distinct stages with increasingly heavy reductions: from 0 to 4 B. and S. numbers no ears are formed; from 4 to 12 B. and S. numbers, four ears, increasing in height; from 12 to 16 B. and S. numbers, four ears decreasing in height; from 16 to 22 B. and S. numbers, six ears increasing in height; and from 22 to 31 B. and S. numbers, four ears increasing in height. With the 500°C. final anneal the curve is shifted toward lower ear heights, and, while the six-ear stage is present at about the same reductions, the ear heights steadily increase from the lowest to the highest reductions. With a 500°C. ready-to-finish and 650°C. final anneal the curve has the same shape as for the 650°/650° group, but ear heights are considerably greater. With 500°C. anneals both before and after the reductions, the height of ear steadily increases with increasing reductions. Neither of the series with the 500°C. ready-to-finish anneal shows the six-ear form.

Fundamentally, any cold reduction at any stage of the production schedule tends to have the effect on directionality indicated in Fig. 8. However, the material being rolled may itself initially have any amount of directionality as a result of previous treatment, and the effect of rolling will vary greatly with this factor.

Temperature of Processing and Final Anneals.—Although annealing temperature is a practical and convenient variable to discuss, it must be understood that the attendant grain size is the factor that actually influences the behavior of the metal.

strip. Clearance between punch and die was equal to the thickness of the strip.

A qualitative guide to the relative importance of this factor is furnished by data obtained in numerous laboratory studies of specific schedules. Fig. 8, while dealing

cent zinc alloys,* shows the effect of varying temperatures at the various anneal points on material produced with reductions throughout of 4 to 6 B. and S. num-

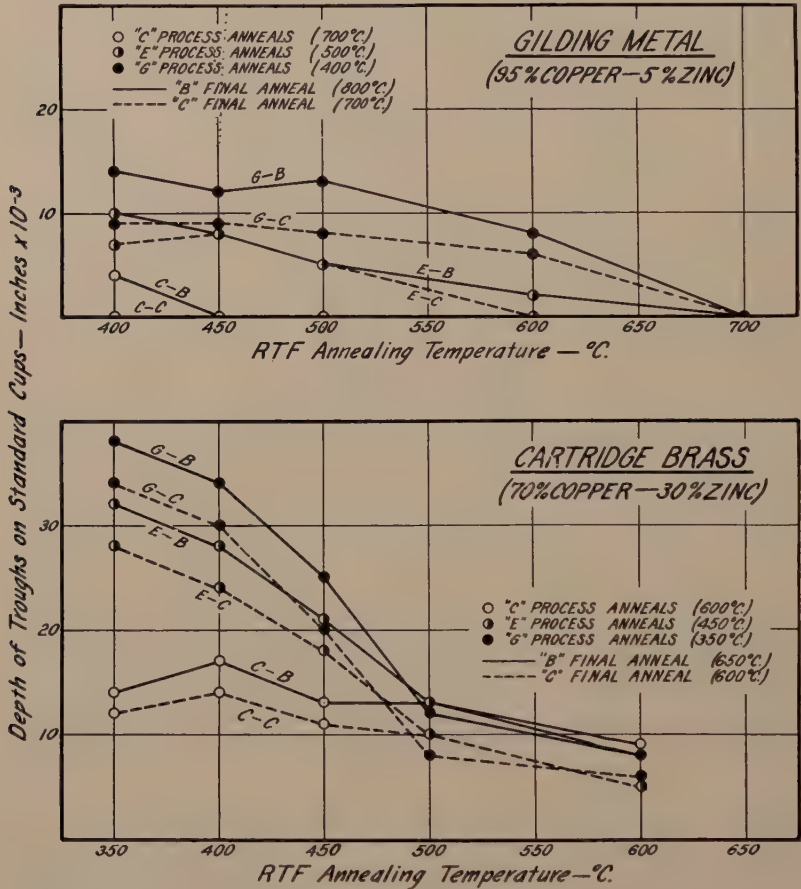


FIG. 9.—EFFECT OF VARIATION IN ANNEALING PRACTICE ON EARING OF 70-30 BRASS AND 95-5 GILDING.

Gilding was given process anneals at stated temperatures at each of the gauges 0.160, 0.100, and 0.064 in., ready-to-finish anneals (plotted as ordinates) at 0.040, and final anneals at 0.020-in. gauge. The 70-30 brass was given process anneals at 0.160, 0.100 and 0.050 in.; ready-to-finish anneals at 0.033 and final anneals at 0.020 in. Both materials previously annealed to 0.10-mm. grain size at 0.320 inch.

primarily with varying reductions, shows also the increase in ear height of the 650°C. final anneal over the 500°C. anneal. So, too, the curve is displaced toward higher ears by the lower ready-to-finish anneal. Fig. 9, with groups of curves for both 5 and 31 per

bers. The overwhelming importance of ready-to-finish annealing temperature is apparent in all cases.

* The cups referred to in Figs. 9 to 15 were 0.300-in. dia. and about 0.250 in. high. They were made from 0.550-in. dia. blanks of 0.020-in. or 0.009-in. gauge as stated.

Fig. 10a gives curves of ear height vs. final annealing temperature for 5 per cent zinc gilding rolled 12 B. and S. numbers at both ready-to-finish and final stages of re-

duction is 26 numbers (from 0.400 to 0.020 in.), variously divided between the ready-to-finish and final reductions by giving the ready-to-finish anneal at the

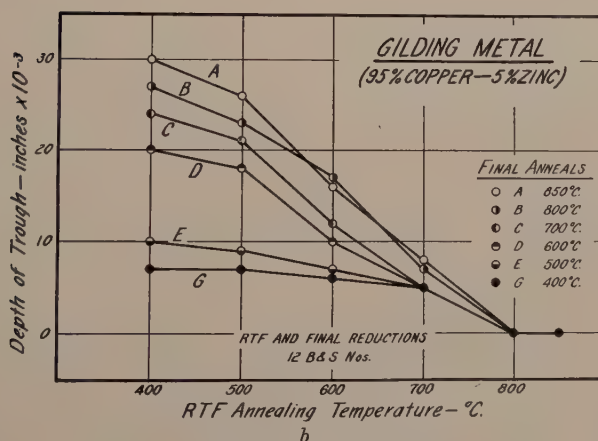
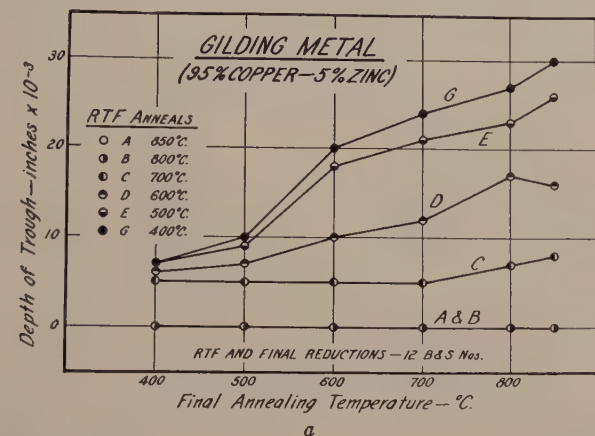


FIG. 10.—EFFECT OF VARIATION IN READY-TO-FINISH AND FINAL ANNEALING TEMPERATURES ON EARING OF 95-5 GILDING.

Rolled 12 B. and S. numbers at both ready-to-finish and final stages. Starting material at 0.320 gauge, 0.100-mm. grain size, rolled to 0.020 in. with single intermediate ready-to-finish anneal at 0.080 inch.

duction. Fig. 10b presents the same data, plotted as a function of the ready-to-finish annealing temperature. Figs. 11a and 11b show the results of a similar series of cups made from 65-35 brass. Fig. 12, referring to a 95-5 gilding, covers, in the top group of curves, material given 12 numbers ready-to-finish reduction and varying final reductions, while in the bottom group the total

gauge noted. Fig. 13 shows comparable data for a 65-35 brass.

A detailed discussion of these results would be too lengthy for the present paper. They can be summarized, together with all other laboratory and production experience, in the following statements on the effect of annealing temperature on the earing of brass:

1. As long as the material is fully recrystallized, the higher the final annealing temperature, the greater, invariably, is the ear height.*

2. The lower the ready-to-finish annealing temperature, the greater, invariably, is the degree of final directionality. The magnitude of this effect naturally varies widely with the amounts of ready-to-finish and final reductions involved.

3. The lower the temperature of the running-down anneals, the greater will be the directionality after any final anneal. This is true for schedules involving reductions up to 8 B. and S. numbers between anneals, but is not always true where very high reductions are involved.

Rolling fine-grained annealed material results in the continued development of a still higher directionality. Ears far higher than those obtainable with the heaviest straight rolling may be developed in brass rolled with only 4 to 6 B. and S. numbers reduction by a succession of intermediate anneals at a low temperature (350° to 450°C.).

SCHEDULES DEVELOPED TO MINIMIZE EARING WITH HEAVY REDUCTIONS

With the ordinary two-high rolls about 20 in. in diameter, it was uneconomical to roll brass more than about 6 B. and S. numbers without annealing. Under these conditions, when earing occurred it was inevitably a result of low processing anneals, and if the ready-to-finish annealing temperature was raised the ears disappeared. The recent introduction of four-high rolls permits very heavy reductions between anneals and makes "earing tend-

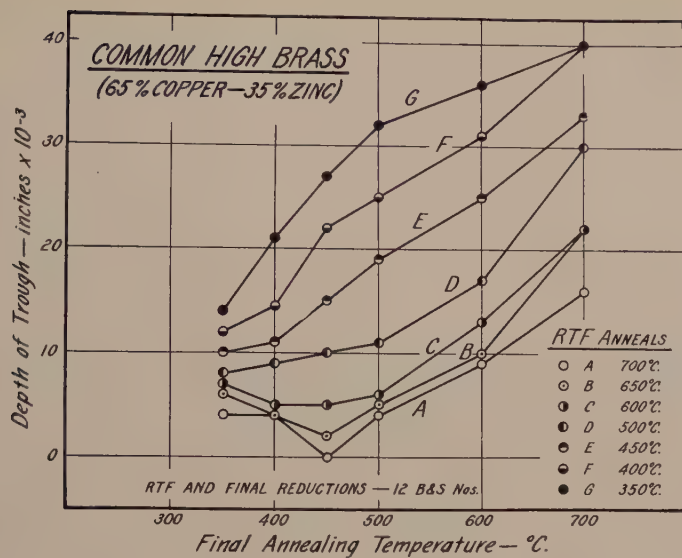
ency" a factor of far greater importance than heretofore in the production of brass for deep drawing—indeed, it sometimes becomes the factor that renders impossible production schedules otherwise highly desirable and economical. Naturally, a search has been made for methods of utilizing the reduction capacity of the new mills while still avoiding ear formation. Two methods, each of limited applicability, have so far resulted from this search.

1. It has been found that with common high brass and other copper-zinc alloys, the directionality resulting from an amount of reduction up to at least 22 numbers can be thoroughly broken up by a high-temperature anneal (650°C. or above) followed by a light reduction (4 B. and S. numbers). Material so processed will be satisfactorily free from ears after final annealing temperatures up to 575°C., and even after a 650°C. anneal it is acceptable for most applications. The limitations of this method are the difficulty of producing material of satisfactory gauge and surface after the high-temperature ready-to-finish anneal.

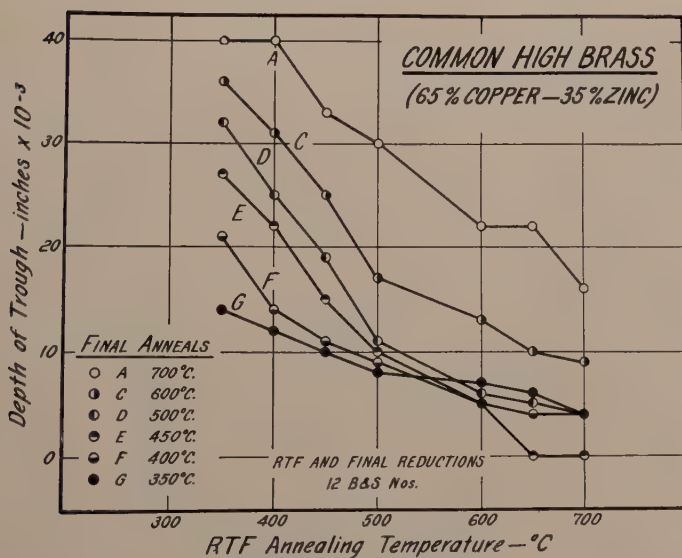
2. It has been found, with 65-35 and other brasses that are to be rolled at least 26 B. and S. numbers from the overhauling point to finish, that this reduction can be made with but a single properly placed intermediate anneal. The importance of properly dividing the reduction is indicated in Figs. 14 and 15, which show data for material finishing from 0.430 to 0.009 in. and 0.020 in., respectively.* A 750°/16 Nos./750°/18 Nos. schedule produces satisfactory strip at 0.009 in., and a 750°/12 Nos./750°/15 Nos. schedule gives satisfactory strip at 0.020 in., for the usual range of final annealing temperature. When the intermediate annealing point is properly chosen, it has been found that the

* X-ray diffraction patterns generally show less directionality as the grain size increases. This is chiefly a result of the fact that insufficient grains are included unless a large area of sample is moved across the X-ray beam. At present it is impossible to state whether the increasing ear height is a result of actual increasing preferred orientation or is an effect solely of grain size or grain boundary.

* It should be pointed out that for the data of Figs. 14 and 15 no attempt was made to measure depths of trough less than 0.005 in., since the large-grain-size samples showed a roughness about the rim of approximately this order of magnitude.



a



b

FIG. 11.—EFFECT OF VARIATION IN READY-TO-FINISH AND FINAL ANNEALING TEMPERATURES ON EARING OF 65-35 BRASS.

Rolled 12 B. and S. numbers at both ready-to-finish and final stages. Starting material at 0.320 gauge 0.100-mm. grain size, rolled to 0.020 in. with single intermediate ready-to-finish anneal at 0.080 inch.

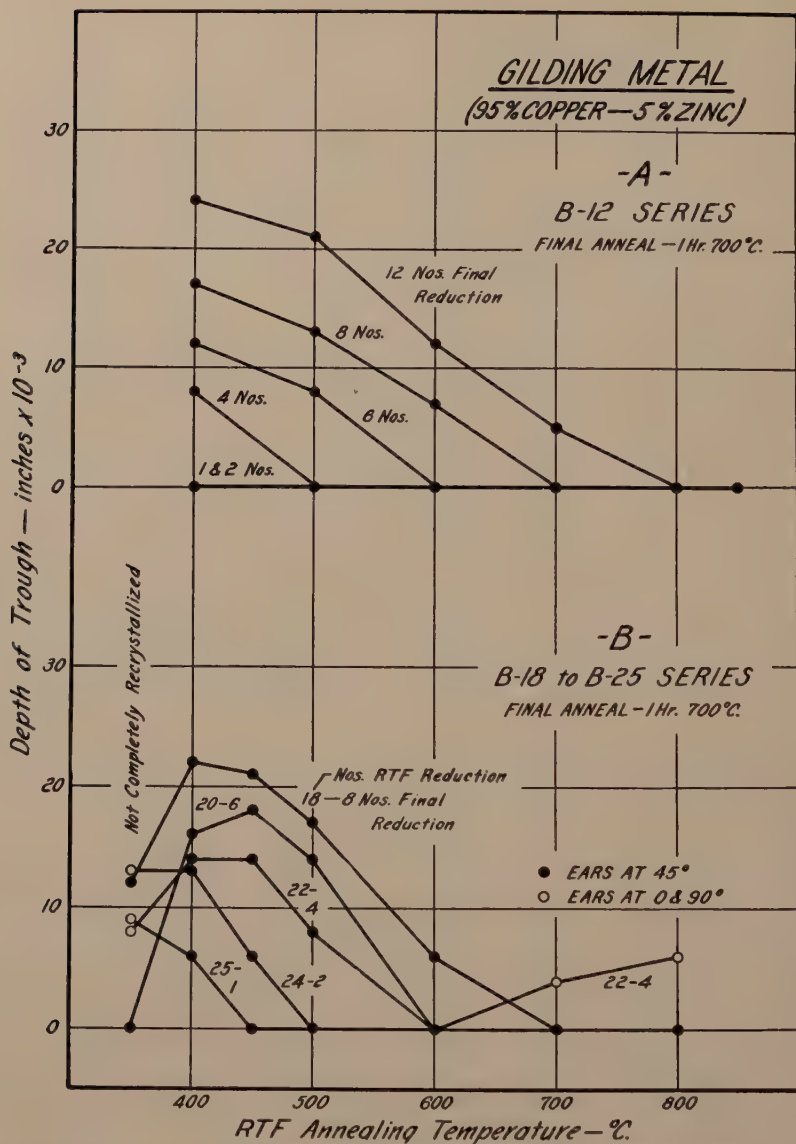


FIG. 12.—EFFECT OF VARIATION IN READY-TO-FINISH ANNEALING TEMPERATURE ON EARING OF 95-5 GILDING.

A. Rolled 12 B. and S. numbers at ready-to-finish stage, and from 1 to 12 numbers at final stage to 0.020-in. gauge. Final anneal, 700°C. in all cases. Pre-ready-to-finish anneal gave grain size 0.100 millimeters.

B. Rolled 26 B. and S. numbers total, the ready-to-finish reductions varying from 18 to 25 numbers and the final from 8 to 1 numbers. Final anneal, 700°C. Material at 0.400-in. gauge, 0.120-mm. grain size, rolled to 0.020 in. with intermediate anneal at reductions and temperatures shown.

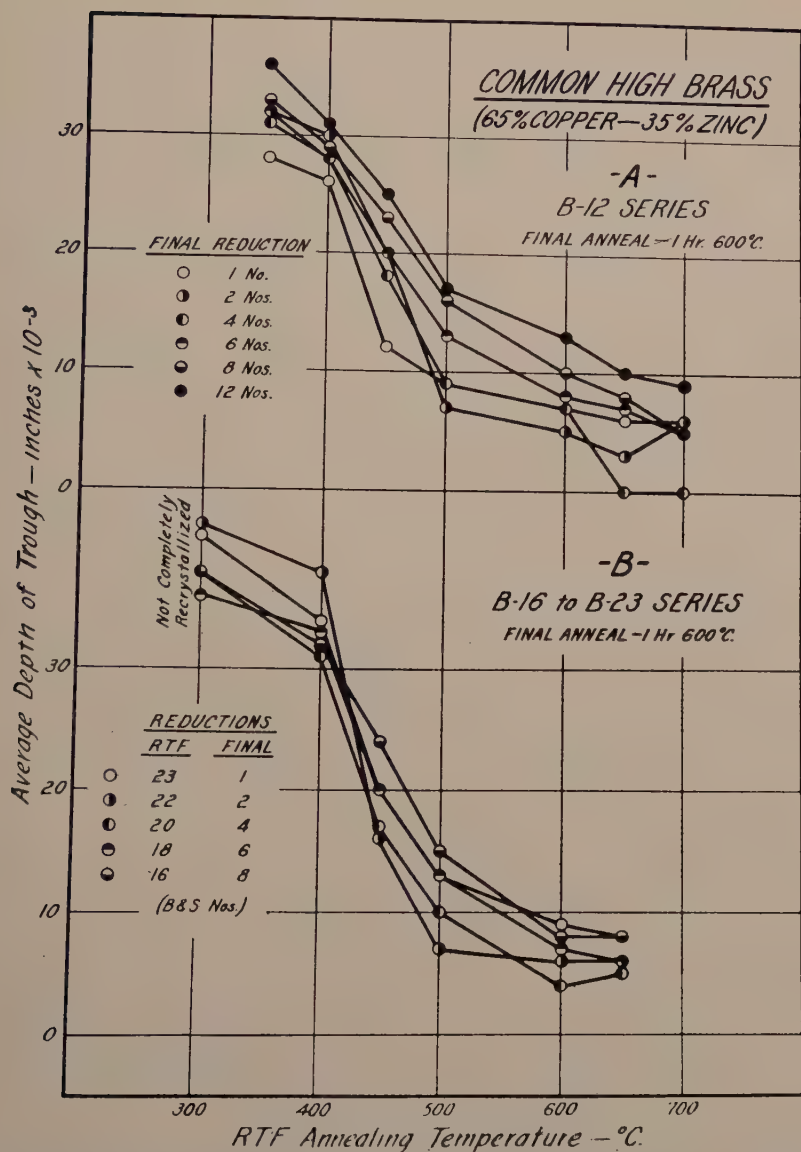


FIG. 13.—EFFECT OF VARIATION IN READY-TO-FINISH ANNEALING TEMPERATURE ON EARING OF 65-35 BRASS.

A. Treatment same as Fig. 12A, except final anneal at 600°C.

B. Rolled 24 B. and S. numbers total, the ready-to-finish reductions varying from 16 to 23 numbers, and the final from 8 to 1 numbers. Final anneal 600°C. Material at 0.320-in. gauge, 0.100-mm. grain size, rolled to 0.020 in. with intermediate anneal at reductions and temperatures shown.

ready-to-finish annealing temperatures may vary somewhat without giving rise to objectionable ears, providing the final anneal temperature is not too high. For

material if equipment is available to give the heavy reductions required and to handle thick, hard metal. Such schedules produce material that is actually somewhat direc-

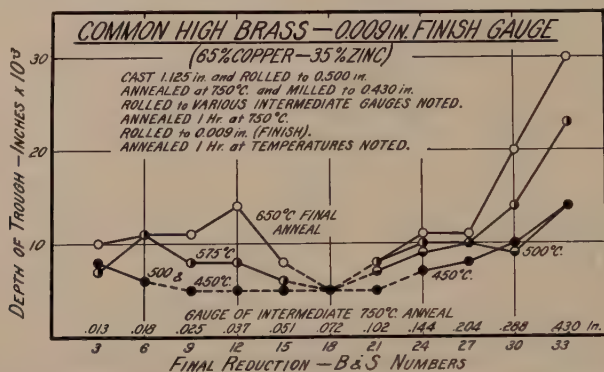


FIG. 14.—EFFECT OF GAUGE OF READY-TO-FINISH ANNEAL ON EARING OF HEAVILY ROLLED 65-35 BRASS (0.009-IN. GAUGE).

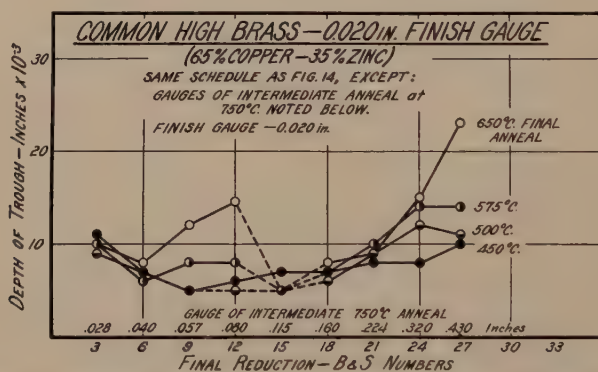


FIG. 15.—EFFECT OF GAUGE OF READY-TO-FINISH ANNEAL ON EARING OF HEAVILY ROLLED 65-35 BRASS (0.020-IN. GAUGE).

example, the material tested for Fig. 7, given an intermediate anneal at about 700°C. at 0.128-in. gauge and finished at 0.020 in., had no ears after a 500°C. anneal, but showed an 0.021-in. ear (on a 0.5-in. dia. cup, not comparable with the 0.300-in. dia. cups of Fig. 15) after a 700°C. anneal. Variation from the optimum intermediate gauge in these schedules is apt to be dangerous, and the entire schedule must be planned at the beginning and adhered to.

This method of rolling is obviously not suitable for odd lots, but is promising for the production of large quantities of ma-

tional, although not in such a manner as to produce ears. Brass so processed possesses normal ductility for a given grain size (Fig. 7).

CONCLUSION

While the effects on earing of the important individual production variables are described in some detail in the foregoing pages, it must be pointed out that prediction of the earing tendency that will result from a given production schedule is not always possible. Each factor influences the others to a greater or less extent, and

no simple rules of behavior can have universal application. In general, the various factors will operate in the manner described herein, but only a cupping test on a trial lot of strip can evaluate the summation of their effects.

ACKNOWLEDGMENTS

The work described herein was instigated by the late Mr. H. C. Jennison and continued under the general direction of Mr. J. R. Freeman, Jr., Technical Manager of the American Brass Co., whose encouragement and valuable advice it is a pleasure to acknowledge. Consultation on production requirements with Mr. R. E. Bassett, Manufacturing Manager of the American Brass Co., has continually been of great value, and the heavy-reduction nonearing schedule was an outcome of his suggestions. The technical supervisors of the Naugatuck Valley mills of the American Brass Co., in particular Messrs. F. N. Meyer, R. S. Baker and the late H. L. Pierson, were of great assistance, not only in getting seemingly impossible rolling schedules tried under commercial conditions but also by contributing liberally from their knowledge and experience in brass-mill practice.

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DISCUSSION

(L. S. Fletcher presiding)

H. E. STAUSS,* Newark, N. J.—It has been a pleasure to read this report. Earing is not one of the major problems with the platinum metals, but we do have difficulties that stem from directionality in the metal. Our solution is always to develop a small grain size in comparison with specimen size, and this procedure has been sufficient for our needs. In this report the authors show that mere small grain size alone is not sufficient to solve their difficulty. Instead, they find that a low final annealing temperature, which would produce small grains, combined with proper higher ready-to-finish annealing temperatures are required to remove earing. These higher earlier temperatures are a bit difficult to understand.

It is recognized that directionality in metal may be introduced by a nonuniformity in structure, such as arises from coring or streaks of inclusions and additional phases. The photomicrographs of Fig. 3 suggest to one who has had no experience with brass but considerable with many other alloys that the metal is not completely homogeneous. There are clusters of small grains and groups of large ones. This fact suggests a somewhat irregular distribution of the component elements, such as might result from absorbing the original prominently cored structure of the casting without diffusing the components uniformly through the alloy.

The fabricating schedule set up by the authors, high ready-to-finish anneal and low final anneal, would appear to be one special method of increasing diffusion in one of the earlier stages of working and of producing a small grain size at finish. Is it possible that deliberate efforts to induce thorough diffusion and uniformity as early in the history of the bar as is possible, followed by control of grain size in the later stages of working, would also achieve the result of reducing earing?

E. W. PALMER AND C. S. SMITH (authors' reply).—Dr. Stauss suggests that lack of chemical homogeneity may be a contributing factor in the earing of brass. Our paper is concerned almost entirely with the directionality resulting from crystallographic alignment

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—the major cause of earing in commercial brass—and we do not believe that other types of directionality have influenced our results to an important extent. The base material used was essentially homogeneous, for it had been given at least two soaking anneals with intermediate rolling before the treatments described in the paper. It is quite true that the persistence of coring, or any other structural feature giving rise to mechanical fiber, may result in directionality. The somewhat uneven grain size of Fig. 3 was caused not by a residual cored structure, but rather by the combination of a low-temperature ready-to finish anneal ($350^{\circ}\text{C}.$), a moderate final cold reduction

(4 B. and S. numbers), and a final anneal at a temperature ($500^{\circ}\text{C}.$) where accelerated grain growth was just beginning. Any effect of composition differences in the casting (1.125 in. thick) would be greatly elongated in this longitudinal section of 0.033-in. strip.

It would indeed greatly reduce the brass mills' earing problems if all customers could use material with a small grain size. However, the great variety of mechanical operations employed in the working up of objects from brass strip makes it necessary to provide non-earing material in a variety of grain sizes, large as well as small, so that each customer's particular requirements may be met.

Corrosion of Copper and Alpha Brass—Chemical and Electrochemical Studies

By J. H. HOLLOMON,* STUDENT ASSOCIATE, AND JOHN WULFF,† MEMBER A.I.M.E.

(New York Meeting, February 1942)

THE opinion has been widely held that the corrosion of alpha brass occurs by the selective solution of zinc. As late as 1939, Fink¹ and Evans² suggested that in the initial stage of the corrosion the selective solution of zinc produces copper-rich areas, which subsequently act as cathodes that facilitate the deposition of copper. Previously Abrams³ had shown that most of the copper found on corroded brass was re-deposited and not residual, although he did not consider the nature of the initiation of the corrosion process. Enough data exist to indicate that any metal surface is sufficiently heterogeneous to provide the anodes and cathodes necessary for the initiation of corrosion.^{4,5} Thus, for alpha brass we need postulate not an initial selective solution of zinc, but only the existence of local differences in electrochemical potential. The heterogeneity responsible for potential differences may arise from oxide and other films as well as from alloy concentration gradients. Even though selective corrosion may be possible in some alloy systems, previous data on alpha brass as well as the experimental work reported in this paper do not require this supposition.

Bengough and May,⁶ in a discussion of Abrams' paper, first suggested the addition of small amounts of arsenic (0.03 per cent)

to alpha brass to prevent the redeposition of copper (dezincification). This suggestion was later substantiated by Nixon.⁷ In their studies of the inhibiting influence of arsenic, Evans and Fink were led to the selective-solution hypothesis in order to explain the initial corrosion of such alloys. They believed that an arsenic film covered anode areas and prevented the formation of copper-rich spots capable of acting as cathodes for the deposition of copper. They did not consider, however, the mechanism by which the arsenical film was formed. Bengough and May,⁸ in another publication, suggested that the commonly found gray or black arsenical film may act to: (1) carry oxygen to the brass surface, (2) increase the discharge potential of copper on brass, (3) precipitate cuprous chloride from colloidal suspension in chloride solutions.

Masing⁹ assumed that the film found upon arsenical brass was metallic arsenic. His measurements of hydrogen overvoltage of bulk arsenic led him to believe that the inhibition of dezincification occurs because the overvoltage of a brass surface is lowered by the arsenic film. He reasoned that this film would permit the more rapid reduction of hydrogen at the cathode, which would prevent the redeposition of copper.

In a recent paper,¹⁰ we have pointed out that the film formed during the corrosion of arsenical brass and copper in stagnant solutions is essentially arsenious oxide (As_2O_3),

Manuscript received at the office of the Institute Nov. 29, 1941. Issued as T.P. 1458 in METALS TECHNOLOGY, April 1942.

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¹ References are at the end of the paper.

and suggested that this film is deposited as metallic arsenic but is oxidized in solution and during the process of film examination. These film-structure studies and the experi-

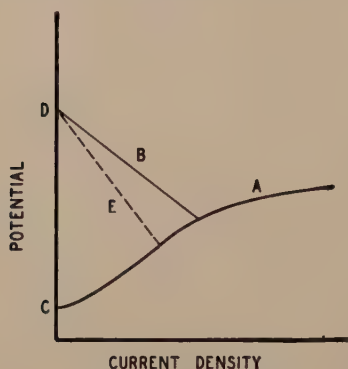


FIG. 1.—POLARIZATION CURVES OF ANODE⁻ (B) AND CATHODE (A).

mental data presented herein do not permit a complete acceptance of the points of view offered by Bengough and May, Masing, or Fink and Evans.

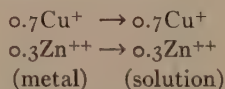
THEORY

Dezincification and its inhibition by arsenic can be explained only by regarding corrosion in aqueous solutions as an electrochemical phenomenon. Local cathodes and anodes on a metal surface permit corrosion to occur. During corrosion, the reaction at the local anodes involves the transfer of positive charge from the metal to the solution while at the cathodes the positive charge is transferred from solution to metal. The anodes thus become negatively charged and the cathodes positively.

During corrosion, current flows between the local anodes and cathodes, and the separate electrode potentials approach the same value.^{11,12} The variation of the electrode potentials with the flow of current is polarization. This occurs primarily at the local anodes if the total anode area is much smaller than the total cathode area, and at the local cathodes if the total cathodic area is relatively small.

A schematic diagram of the current density-potential relationships of the anode and cathode areas is presented in Fig. 1. *A* represents a hypothetical variation of the cathode potential (average of all local cathodes) with current density, while *B* denotes the variation of the anode potential. *C* represents the magnitude of the reversible cathode potential or, in other words, *C* is a measure of the change of free energy during the hypothetical cathode reaction. *D* is the reversible potential of the hypothetical anode reaction. The intersection of curves *B* and *A* determines the corrosion rate and the measured potential. The change in cathode potential with increasing current density is due to an increase in the concentration of positive charge at the cathode or to a "sluggishness" of the cathode reaction. The change in potential resulting from polarization at the local cathodes is usually termed "overvoltage." The polarization at the anode is due to formation of a film or to a decrease in the anode area or to both. The slope of the anode polarization curve measures the resistance in the pores of this film. If the film is continuously formed during corrosion, curve *B* will approach *E*.

During the corrosion of alpha brass, it may be assumed that copper enters the solution as the univalent ion and that zinc enters the solution as the divalent ion. The anode reaction is then



Since the anode reaction that occurs during the corrosion is dependent on the nature of the cathode reaction, the conditions must be determined under which the following cathode reactions occur:

- A. $\text{Cu}^{++} + (e) \rightarrow \text{Cu}^+ (\text{solution})$
- B. $\text{Cu}^+ (\text{solution}) \rightarrow \text{Cu}^+ (\text{metal})$
- C. $2\text{H}^+ + 2(e) \rightarrow \text{H}_2$
- D. $2\text{HNO}_3 + 2(e) \rightarrow 2\text{NO}_2 + \text{H}_2\text{O} + \text{O}^-$
- E. $\text{O}_2 + 2\text{H}_2\text{O} + 4(e) \rightarrow 4\text{OH}^-$

An attempt has been made in the present work to study each reaction separately as far as such study is possible.

mentary X-ray experiments performed by us indicated that the arsenic did not exceed the solubility in any of the alloys

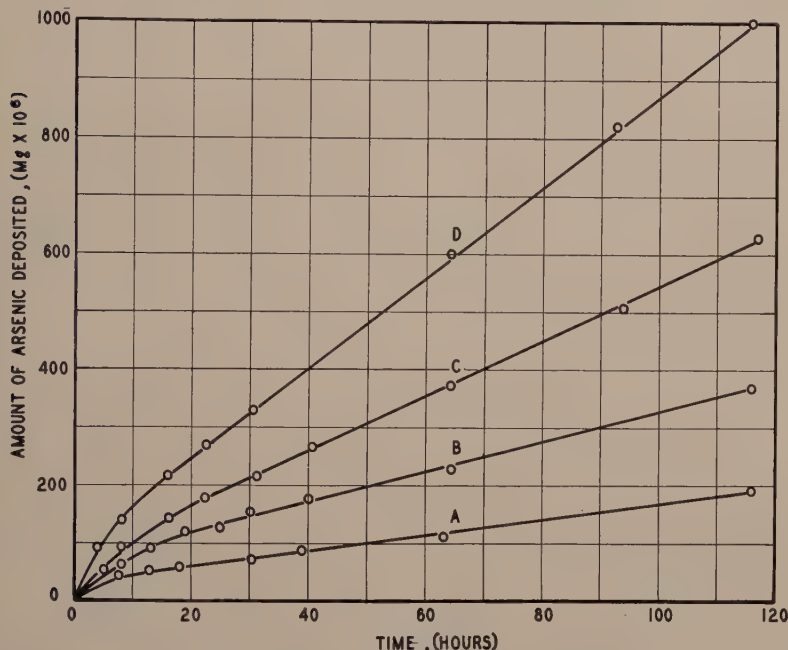
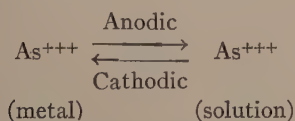


FIG. 2.—AMOUNT OF ARSENIC DEPOSITED AS A FUNCTION OF TIME FROM 2N HYDROCHLORIC ACID SOLUTION CONTAINING 1, 2, 3, AND 4 MILLIGRAMS OF ARSENIC AS H_3AsO_3 , RESPECTIVELY.

For arsenical brass, additional electrode reactions are possible. Among them are:



That the arsenic is actually redeposited from solution is evident from our electron-diffraction work, which confirms the existence of the foregoing reactions during the corrosion of arsenical brass. Subsequent work reported later in the paper lends further support to this contention.

Hume-Rothery¹³ has shown that arsenic occurs in solid solutions of copper as the trivalent ion. It is reasonable to assume that arsenic is also present as the trivalent ion in alpha brass for concentrations below the solubility limit of arsenic. Supple-

used in our experiments. It is also reasonable to assume, therefore, that during corrosion arsenic will enter solution as the trivalent ion.

EXPERIMENTS

Redeposition of Arsenic

Supplementing the electron-diffraction work previously reported, radioactive tracer experiments were performed to demonstrate that arsenic can redeposit upon alpha brass. Arsenic as arsenic trioxide (As_2O_3) was dissolved in 2N HCl. This acid was chosen because it prohibits the precipitation of any copper corrosion products by virtue of its low pH and by its combination with the available copper to form ionic complexes. Part of the arsenic trioxide was radioactive, having been pre-

pared in the Massachusetts Institute of Technology Cyclotron Laboratory.

Four solutions were made up containing 1, 2, 3, and 4 mg., respectively, of arsenic

The curves in Fig. 3 indicate the amount of arsenic deposited upon the brass samples as a function of time. Electron-diffraction patterns taken of the films formed were

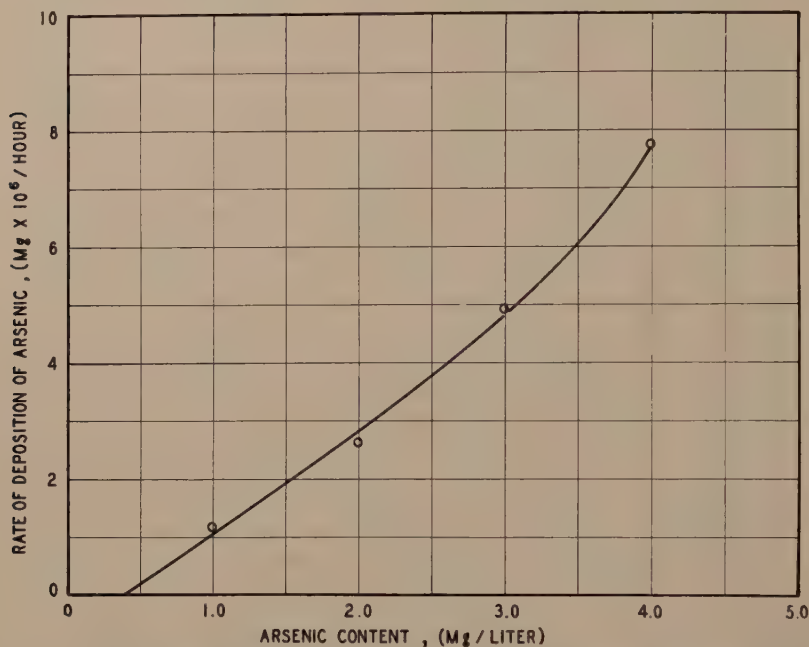


FIG. 3.—RATE OF DEPOSITION OF ARSENIC AS A FUNCTION OF ARSENIC CONTENT FROM 2N HYDROCHLORIC ACID SOLUTIONS.

as arsenic trioxide per liter of solution. Each solution was calibrated with a counter mechanism to determine the amount of radioactive arsenic present per milligram of arsenic. A plain brass sample whose surface area was 1.2 sq. cm. (part of the sample was covered with wax) was immersed in each of the four solutions. The amount of radioactive material on the sample was measured as a function of time. From this determination, the amount of arsenic deposited was ascertained. The samples were removed from the solution for each measurement, quickly washed in distilled water, and dried. Correction for the decay of the radioactivity of the arsenic was made by the use of a standard arsenic sample, which was prepared simultaneously with the solutions.

characteristic of arsenic trioxide. The slopes of the initially straight portion of the curves of Fig. 2 were determined and are plotted in Fig. 3 as a function of the arsenic content of the solution. The curve was extrapolated to zero rate, and the exact concentration of arsenic trioxide necessary for deposition was determined. The potential of plain brass in a stagnant 2N HCl solution can be calculated from this concentration and the standard potential of the reaction: $\text{H}_3\text{AsO}_3 + 3\text{H}^+ + 3(e) \rightarrow \text{As}(s) + 3\text{H}_2\text{O}$. The calculated and measured values are +0.15 volts.

A series of similar experiments was performed in which the solutions contained 10 grams of brass (as copper and zinc chloride) per liter as well as the arsenic as arsenic trioxide. In these solutions the

arsenic, copper, and zinc were in approximately the same ratio as they are found on arsenical brass. The arsenic did not deposit on the brass surface. The radioactive tracer

time, as a function of the arsenic content of the alloy, and in some cases as a function of the concentration of the corrodent. The preparation, composition, and grain size of

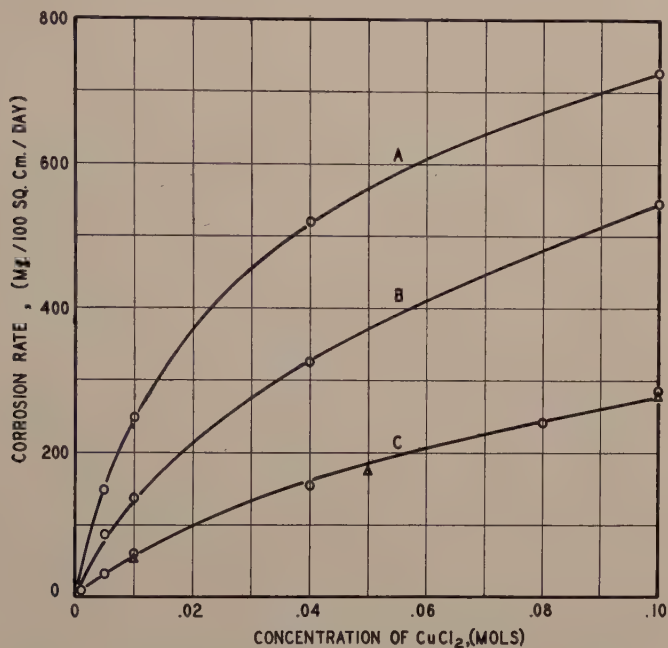


FIG. 4.—RATE OF CORROSION OF BRASS.

Curve C, circles show corrosion of arsenical brass in air-free cupric chloride solution; curve C, triangles represent average rate of corrosion of copper samples; curve B represents rate of corrosion of plain brass as determined by deposition of copper and A represents rate as determined by reduction of cupric-to-cuprous ions.

method did indicate that some of the solution was adsorbed upon the brass surface, but the amount of arsenic present remained constant after the first few minutes of immersion and was calculated to be less than 5×10^{-9} grams.

Corrosion and Potential Studies

The rates of corrosion of brass and copper according to the cathode reactions previously listed were determined. The electrochemical potentials of brass and copper (both containing various percentages of arsenic) were measured in the same media in which the rates were observed. For each reaction, the rates of corrosion and the potentials were determined as a function of

the alloys have been presented previously.¹⁰ All the samples were finished upon a "120" belt and washed in benzene and acetone prior to immersion. For all media except sodium chloride, individual flasks were used for the samples of the same arsenic content. Weight-loss determinations were made by taking the difference between weights before and after corrosion. Usually 16 identical samples were used in order to determine the corrosion rate more accurately.

In most of the experiments, it was necessary to control the atmosphere above the corrodent. Therefore, to remove the air already dissolved in a solution, the desired gas was bubbled through the solution for 6 hr. prior to the immersion of the sample.

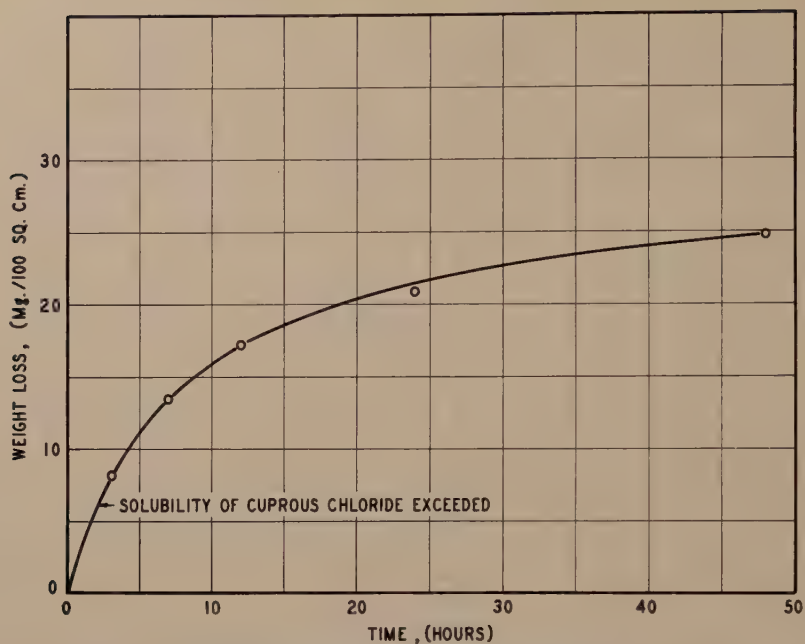


FIG. 5.—AVERAGED WEIGHT LOSS PER UNIT AREA OF ARSENICAL-BRASS SAMPLES AS FUNCTION OF TIME IN 0.005M CUPRIC CHLORIDE SOLUTIONS.

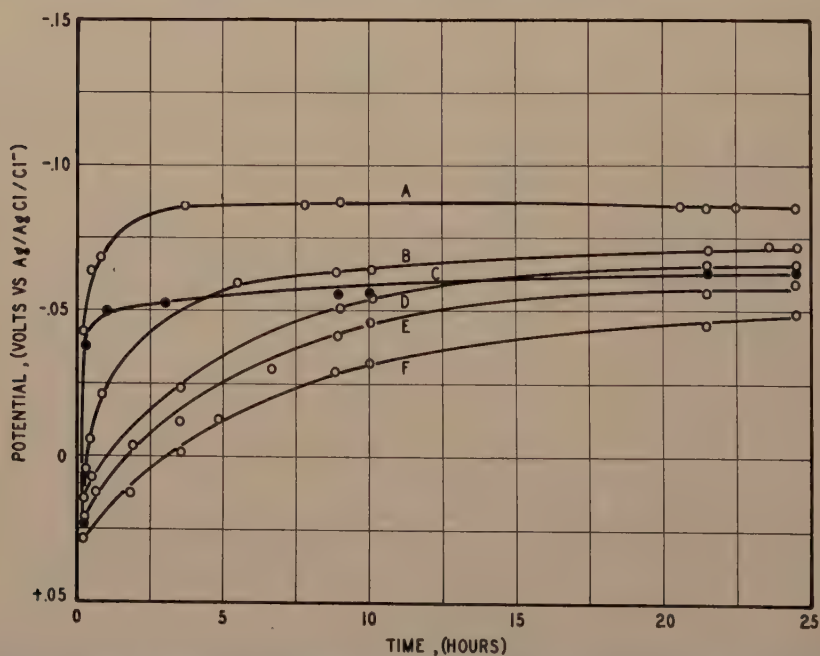


FIG. 6.—TIME-POTENTIAL RELATIONSHIPS IN AIR-FREE 0.1M CUPRIC CHLORIDE SOLUTIONS. A, plain brass; B, brass containing 0.014 per cent As; C, plain copper; D, brass containing 0.024 per cent As; E, 0.045 per cent As; F, 0.248 per cent As.

After the dissolved air was removed, the flasks were flushed with the required gas and the solution was admitted. Without contacting the atmosphere, the solution

were not soluble in water. Hydrochloric acid was used only after it was observed that this washing prior to immersion changed the weight by less than 0.5 mg

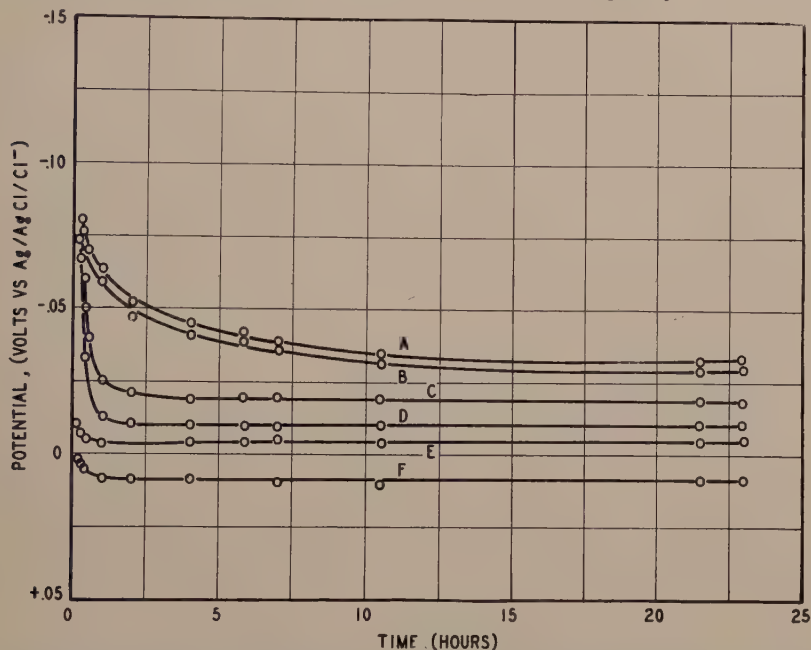


FIG. 7.—TIME-POTENTIAL RELATIONSHIP IN AIR-FREE 0.001M CUPRIC CHLORIDE SOLUTIONS. A, plain copper; B, copper containing 0.013 per cent As; C, 0.084 per cent As; D, 0.206 per cent As; E, 0.413 per cent As; F, 0.603 per cent As.

filled the flasks, which already contained the samples. The nitrogen or hydrogen was then bubbled through the flasks at the rate of about 100 c.c. per min. With corrodents in which gas was evolved at the cathode, the flasks could not be connected in series, for the back-pressure caused by the solution in the preceding flasks was found to vary the corrosion rate in the succeeding flasks. Hence, for the nitric and hydrochloric acid series, the flasks were connected in parallel to the gas outlet. The samples remained in the corrodent for 12 hr., unless otherwise indicated. After removal from the solutions, the samples were washed in normal hydrochloric acid followed by benzene and acetone. Most of the corrosion products were found to be soluble in hydrochloric acid, whereas they

The samples were washed for 30 sec. in this acid and rinsed in water before they were washed in benzene and acetone. The electrochemical data were obtained in a manner essentially similar to that which has been described previously in the literature.¹⁴

Since the primary object in obtaining this electrochemical data was not to procure absolute values, but rather to compare the potentials of the brasses and of the coppers as a function of arsenic content, the cells were constructed so that a number of samples could be measured against the same reference electrode. Eight vertical cells were placed on the periphery of a circular iron stand. The Ag/AgCl/Cl⁻ standard cell was placed in the center of the stand. Thus by means of bridges from

each of the cells, all eight of the potentials were measured against the central electrode. The cells were so constructed that the samples were placed horizontally at

was determined as a function of cupric-ion concentration in solutions containing cupric chloride. The solutions were prepared by dissolving cupric chloride in distilled

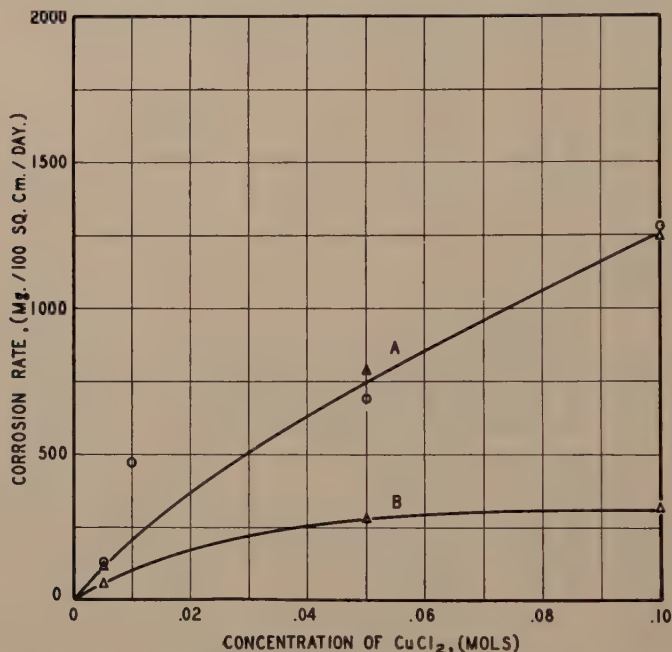


FIG. 8.—RATE OF CORROSION IN AERATED CUPRIC CHLORIDE SOLUTIONS CONTAINING 0.01 MOL OF HYDROCHLORIC ACID PER LITER.

Curve A represents rate of corrosion of both plain and arsenical brasses, as determined by cupric-to-cuprous reduction. Curve B represents rate of corrosion of plain brass due to deposition of copper.

the bottom, while the solution and the gas entrances were at the top. Eight copper samples were put in one such apparatus, while the brasses were placed in another. The two standard cells used were checked frequently against each other, and the variation was not greater than 0.005 volts. This correction was made when necessary. A Leeds and Northrup type K potentiometer and a vacuum-tube galvanometer were used to measure the over-all potential of the complete circuit.

Air-free Cupric-ion Solutions

The rate of the reaction



water. Purified nitrogen was bubbled through the solution prior to immersion of the sample in order to remove the dissolved oxygen and then was bubbled continuously during the corrosion at a rate of 100 c.c. per min. In all the cupric chloride solutions, copper redeposited upon the nonarsenical brass samples. In the more concentrated solutions (above 0.01 M), a slight amount of copper redeposited upon the sample containing 0.014 per cent As. After 12-hr. immersion in the 0.1 M solution, a very small amount of copper was observed even on the samples that contained more than 0.014 per cent As. No significant variation was observed in the evidence of corrosion among the

copper samples except that a steel-gray to black film was formed on all samples containing arsenic. The variation in corrosion noted in a given solution among the

$\text{Zn}(\text{OH})_2$ precipitates. In any case, all of the zinc will remain in the corrodent (either as a solute or as a precipitate), and the actual corrosion rate in terms of the brass

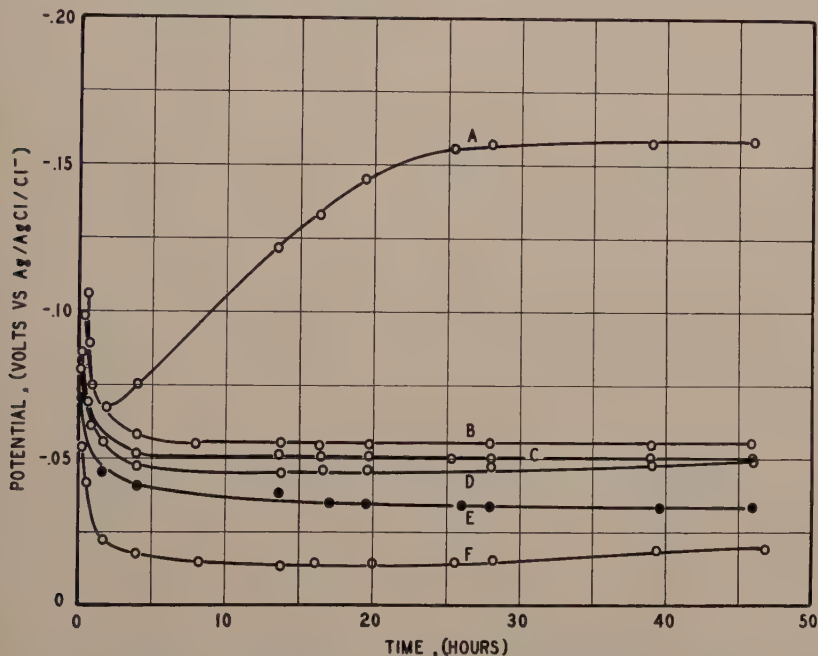


FIG. 9.—TIME-POTENTIAL RELATIONSHIPS IN AERATED 0.01M CUPRIC CHLORIDE SOLUTIONS CONTAINING 0.01 MOL HYDROCHLORIC ACID PER LITER.

Curve A, plain brass; B, brass containing 0.024 per cent As; C, 0.045 per cent As; D, 0.087 per cent As; E, plain copper; F, brass containing 0.248 per cent As.

various arsenical brasses and among the various copper samples was less than 10 per cent. The data for arsenical brasses and all of the coppers, therefore, were plotted as an average of all the samples.

Curve C of Fig. 4 represents the rates of corrosion of both arsenical brass and copper as determined by the cupric to cuprous ion reduction. The rates of corrosion of arsenical brass and copper are the same for all cupric-ion concentrations.

The rate of corrosion of plain brass in air-free cupric-ion solutions cannot be determined by means of direct weighing, because copper is redeposited during the corrosion process. The zinc ions released during the corrosion remain in the solution as the chloride unless the pH is such that

that is lost may be determined from the amount of zinc in solution.* Curves A and B of Fig. 4 include the data for the corrosion rate of plain brass as determined by the two

* The actual weight loss may be determined by subtracting the final weight from the original weight:

$$O \text{ (original)} - F \text{ (final)} = W \text{ (weight loss)}$$

$$F = W' \text{ (weight corroded brass)} + C \text{ (copper redeposited)}$$

$$W' = O - B \text{ (brass dissolved; determined by zinc analysis)}$$

$$O - F = W$$

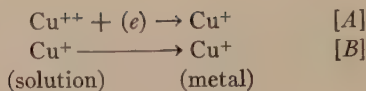
$$F = W' + C$$

$$W' = O - B$$

$$B - W = C$$

The amount of copper deposited is equal to the amount of brass dissolved minus the actual weight loss.

reactions:



The data in these two curves are expressed

chemical relationships among the various alloys. Fig. 6 illustrates the change of potential of different arsenical brasses in air-free 0.1M cupric chloride solutions as a function of time. The potentials of all of the alloys decrease initially and approach

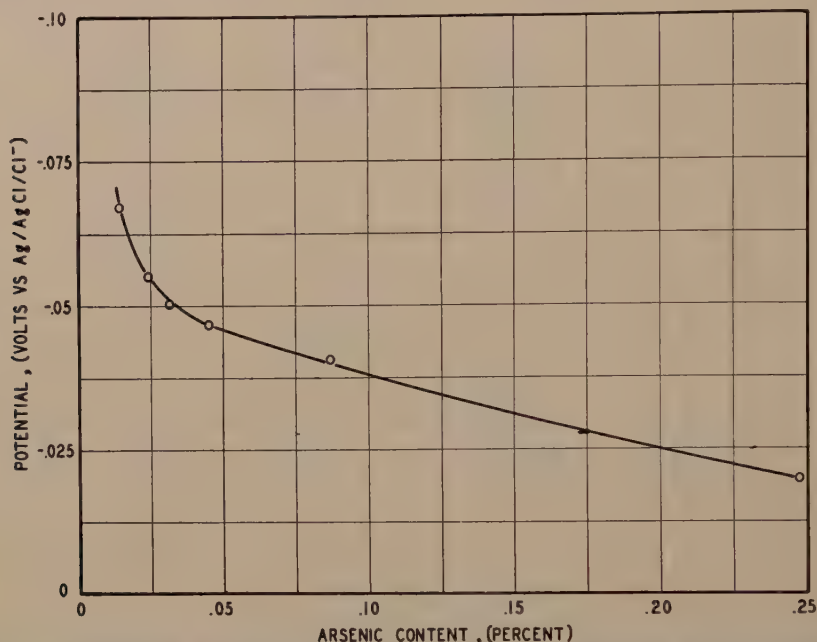


FIG. 10.—POTENTIAL OF BRASS AS FUNCTION OF ARSENIC CONTENT AFTER 16 HOURS IMMERSION IN AERATED 0.01M CUPRIC CHLORIDE SOLUTIONS CONTAINING 0.01 MOL OF HYDROCHLORIC ACID PER LITER.

in terms of the weight loss of the brass. (The amount of brass is determined by calculating the weight equivalent of brass lost per gram of copper redeposited. If this weight is subtracted from the loss as determined by the zinc analyses of the solution, the loss equivalent to the cupric-to-cuprous reduction results.) In Fig. 5 the averaged weight losses of the arsenical brass samples when immersed in 0.005M cupric chloride are plotted as a function of time. The corrodent becomes saturated in cuprous chloride after 2 hr. and the corrosion rate decreases.

Time-potential studies were made in the same solutions to ascertain the electro-

steady-state values, which become more positive with increasing arsenic content. The steady-state potential of plain copper (curve C) is approximately that of a brass containing 0.024 per cent As (curve D). In order to demonstrate that the electrochemical behavior of arsenical copper is similar to that of arsenical brass, the data for arsenical coppers in 0.001M cupric chloride solutions are presented in Fig. 7. The dependence of the potentials on arsenic content of the copper alloys is analogous to the brasses. In one, however, the initial variation is toward positive values, while in the other it is toward negative values.

Aerated Cupric-ion Solutions

The previous studies of corrosion in air-free solutions are helpful in ascertaining the mechanism of the corrosion of brass

the precipitation of $\text{Zn}(\text{OH})_2$, Cu_2O , or $\text{Cu}(\text{OH})_2$.

In aerated solutions the rate of corrosion is increased by the continuous regeneration

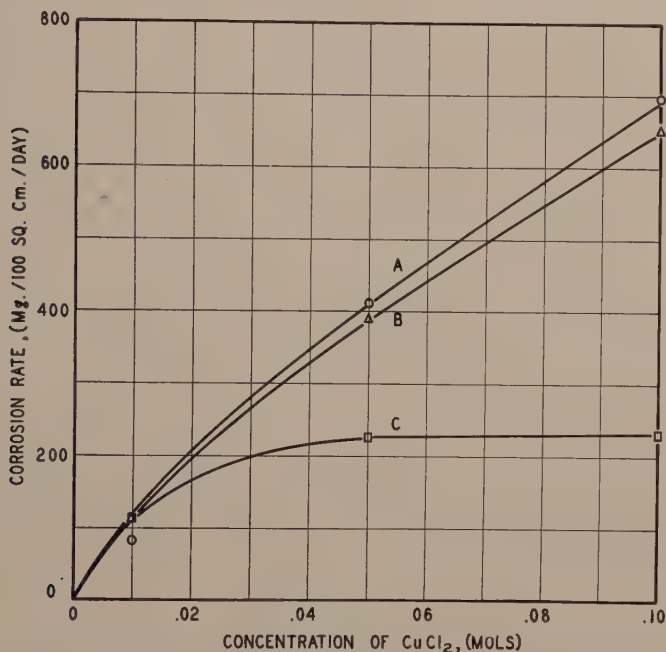
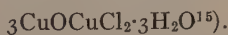


FIG. 11.—CORROSION RATE IN AERATED CUPRIC CHLORIDE SOLUTIONS.

Curve B represents corrosion rate of arsenical brasses; curve A, corrosion rate of plain brass as determined by cupric-to-cuprous reduction and curve C, as determined by copper deposition.

in aerated solutions. The behavior in these solutions approximates that met in practice. Brass tubes usually corrode initially according to Eq. E. The cuprous ion produced at the anode is oxidized to cupric ion by dissolved oxygen. Thereafter, the corrodent is essentially an aerated cupric-ion solution. Air was bubbled through solutions containing various concentrations of cupric chloride. The oxygen dissolved in the solution performs several functions:

1. It oxidizes cuprous to cupric ion.
2. It causes the precipitation of the basic chloride ($\text{Cu}_4(\text{OH})_6\text{Cl}_2 \cdot \text{H}_2\text{O}^8$ or



3. It is reduced at the cathode to hydroxyl ions. This hydroxyl ion may cause

of the cupric ion. If the cupric ion is precipitated as the basic chloride, the effect is negligible. In order to avoid the precipitation of basic chloride, the solutions were made 0.01 molal in hydrochloric acid. The corrosion rate in these solutions is greater than that found in the air-free solutions. Fig. 8 illustrates this behavior. Curve A represents the corrosion rate as determined by the cupric-to-cuprous reaction. The rate is much greater than curve C of Fig. 4. Curve B is the rate of corrosion as determined by the cuprous-to-copper reduction (amount of copper deposition). The rate of this reaction is markedly reduced by the addition of air to the solutions. The part of the corrosion of

plain brass that is determined by the reduction of the cupric-to-cuprous ions is unaffected by the deposition of copper. The curves in Fig. 9 illustrate the variation

of the brass samples are plotted as a function of the concentration of cupric chloride in such solutions. The rate of corrosion of the arsenical brass in these solutions is the

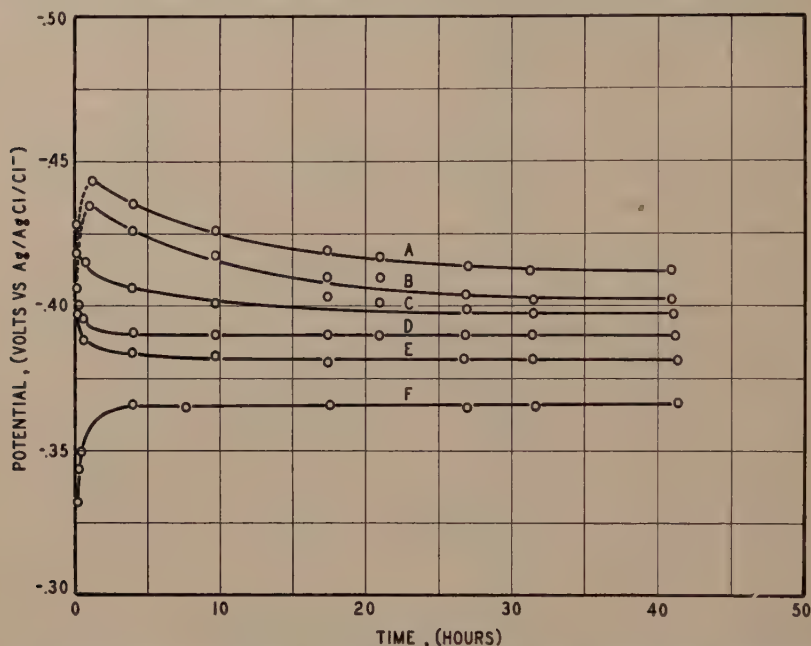


FIG. 12.—TIME-POTENTIAL STUDIES IN 6N HYDROCHLORIC ACID UNDER ONE ATMOSPHERE OF HYDROGEN.

Curve A, plain brass; B, brass containing 0.024 per cent As; C, 0.045 per cent As; D, 0.087 per cent As; E, 0.256 per cent As; F, 0.425 per cent As.

of potential with time in aerated acidic cupric chloride solutions (0.01M) for the arsenical brasses.

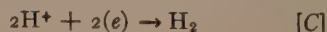
The effect of arsenic upon the steady-state potential is illustrated in Fig. 10. In this curve, the variation of the potential after 16-hr. immersion in the solution is plotted as a function of the arsenic content. The curve is representative of all the potential data for the arsenical brasses after the steady state is reached. Variations of the electrolyte do not change the general form of the curve of Fig. 10. Arsenic in the alloy raises the steady-state electrochemical potential in any solution.

Basic cupric chloride precipitates during corrosion in acid-free cupric chloride solutions. In Fig. 11, the rates of corrosion

same as the rate of corrosion of plain brass as determined by the cupric-to-cuprous reduction. The arsenic film simply prevents one cathode reaction, leaving the rate of the other unaffected. The rate of deposition of the copper increases rapidly up to about 0.04M cupric chloride and for higher concentrations remains constant. The rate of corrosion of arsenical brass in aerated acid solutions is less than in acid-free solutions according to Figs. 11 and 8. The rate in aerated acid solutions is greater than in air-free solutions (Figs. 11 and 4).

Hydrochloric Acid Solutions

Another reaction that may occur at local cathodes during the corrosion of brass is



The electrochemical nature of copper and of alpha brass does not permit this reaction in solutions in which the hydrogen-ion con-

appears to be dependent upon the arsenic content of the alloys. The variation of the steady-state potential is essentially the

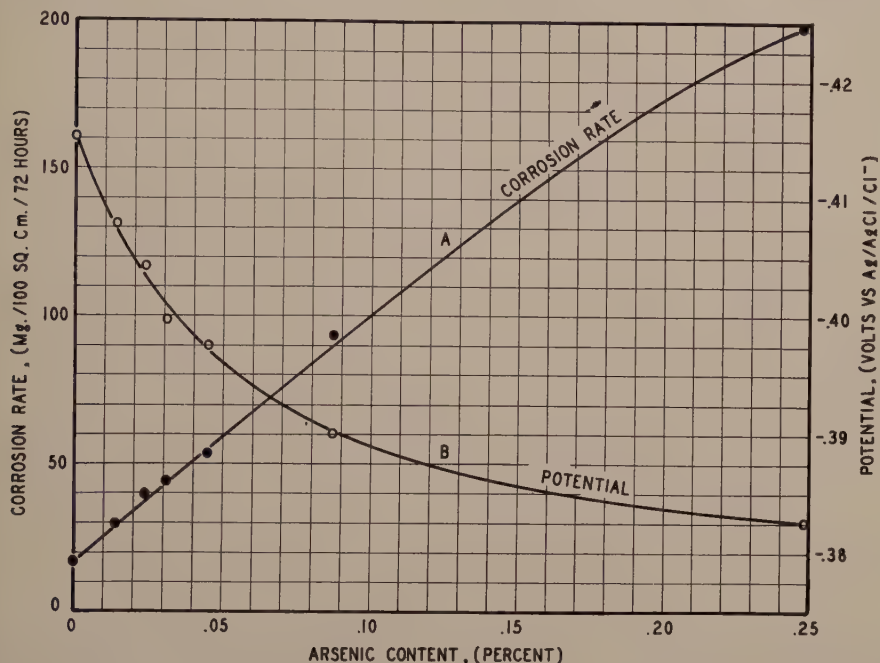
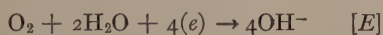


FIG. 13.—CORROSION RATE AND POTENTIAL AS FUNCTION OF ARSENIC CONTENT OF ALPHA BRASS IN 6N HYDROCHLORIC ACID UNDER ONE ATMOSPHERE OF HYDROGEN.

centration is very low. In aerated weak acid solutions, the redox reaction



predominates and the corrosion depends upon the rate of diffusion of oxygen to the interface. In very strong acid solutions (above 5N), however, this reaction may be induced. Since the reduction of hydrogen ion is controlled by an overvoltage mechanism, the corrosion rate and the potential are dependent on the pressure of hydrogen above the solution.¹⁶ Since hydrogen was bubbled through the corrosion cells and the potential cells, the partial pressure of hydrogen was maintained at one atmosphere. The potential data are presented in Fig. 12. All of the potentials are more negative than those of the previous sections. The initial variation of the potential

same as that found in the cupric chloride solutions and is presented as curve B of Fig. 13. The corrosion rate of the brass in the hydrochloric acid solution is plotted as curve A in Fig. 13 as a function of arsenic content. Experimental evidence obtained by others¹⁷ indicates that the hydrogen overvoltage should be a linear function of the logarithm of the current density (or corrosion rate). Fig. 14 illustrates such a linear relationship.

Since gas is evolved when alpha brass is immersed in nitric acid solutions, the corrosion rate may be governed by an overvoltage mechanism. The increase in the rate of corrosion with arsenic content in $\frac{1}{2}$ N HNO_3 solutions is illustrated in Fig. 15. The steady-state potential curves of the brasses in this solution are of the same form as those found in hydrochloric acid.

Aerated Sodium Chloride Solutions

The corrosion of copper in aerated salt solutions is governed by overvoltage, whereas the corrosion of brass is wholly

tain arsenic and copper in the same ratio as found in arsenical brass. This result is in agreement with the work of Bengough and May,⁸ who immersed nonarsenical alpha-



FIG. 14.—POTENTIAL OF ARSENICAL BRASS IN 6N HYDROCHLORIC ACID AS FUNCTION OF LOGARITHM OF CORROSION RATE.

dependent upon the rate at which oxygen reaches the interface.¹⁸ Fig. 16 illustrates the rate of corrosion in aerated 4 per cent sodium chloride solution as a function of arsenic alloy content. The rate decreases markedly to 0.084 per cent As and appears to have a minimum between 0.084 and 0.248 per cent As. The rate of corrosion of plain copper in this solution is approximately 80 mg. per 100 sq. cm. per day.

DISCUSSION OF RESULTS

The electron diffraction and the radioactive tracer experiments show that, during corrosion, arsenical brass dissolves as an entity and metallic arsenic subsequently redeposits. The radioactive tracer experiments indicate that in most solutions the potential of the brass surface allows the deposition of arsenic. Arsenic, however, does not deposit from solutions that con-

tain arsenic and copper in the same ratio as found in arsenical brass. They found that arsenic deposited only when the ratio of arsenic to copper was approximately one. All the data now indicate that the arsenic combines with copper in solution to form an arsenite, CuHASO_3 or $\text{Cu}_3(\text{AsO}_3)_2$, thus preventing the arsenic ions from reaching the cathode. The arsenic that leaves arsenical brass during corrosion exists at the metal-solution interface as the trivalent ion, since it occurs in the metal lattice as this ion¹³ and as such may redeposit at local cathodes.

The patterns of the films formed during corrosion and during the radioactive experiment were characteristic of arsenious oxide. This result is to be expected, since the technique employed permits contact of the

film with the oxygen of the corrodent and the atmosphere. The electrons that produce the pattern penetrate only about 100 \AA .¹⁹ of the film; hence an appreciable part of it

is greater the higher the arsenic content, for at a given time the film is more nearly complete. The more nearly complete the film, the greater the IR^* drop in the pores

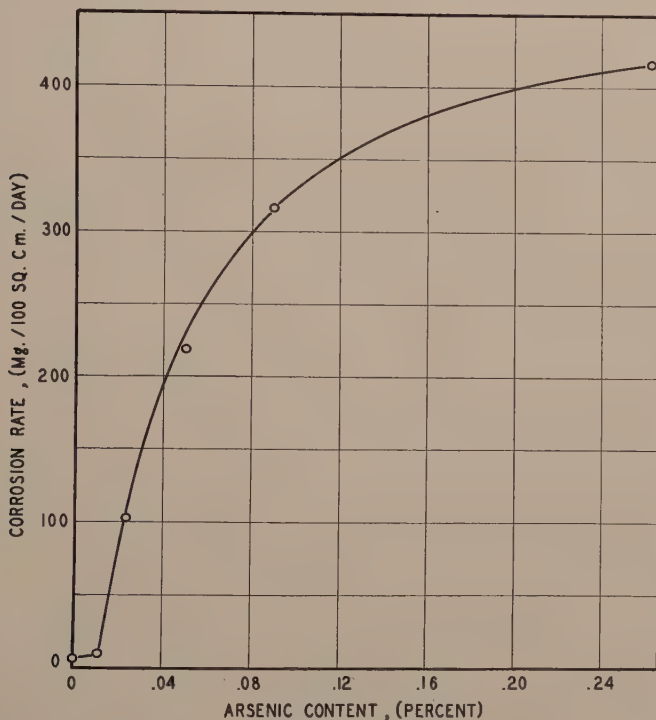


FIG. 15.—CORROSION RATE IN $\frac{1}{2}N$ NITRIC ACID SOLUTION AS FUNCTION OF ARSENIC CONTENT OF BRASS.

may well consist of metallic arsenic. Indeed, films formed on plain brass when immersed in arsenious acid solutions exhibit electron-diffraction patterns characteristic of the oxide and back-reflection X-ray patterns characteristic of metallic arsenic.

The formation of the arsenical film during corrosion of arsenical coppers and brasses alters the electrochemical characteristics of the metal. The electrochemical potential at a given time in all cases is more positive the higher the arsenic content of the alloy. As a result of our experiments with brass, however, there seem to be three different aspects of the increased potential. In cupric chloride solutions, the potential

of the film and hence the more positive the measured potential. The increase in potential with increasing arsenic content might be due to a change in the potential of the brass per se and not wholly to the formation of an arsenical film. In 2-molal dichromate solutions, the potential is quite positive and a film does not form during corrosion. Supplementary experiments indicate that in these solutions there is only a slight dependence of potential upon arsenic content. Therefore, the increase in potential is primarily due to the formation of the arsenical film and the subsequent increase of pore resistance.

* This resistance, R , is equivalent to the constant, K_a , used by Brown and Mears.²⁰

In hydrochloric acid solutions, the increased potential may be attributed to a different mechanism.¹ Since Fig. 14¹ exhibits a straight-line relationship between the loga-

pendence sharply on potential. The anode polarization curve of plain brass is denoted by *A* and intersects the oxygen curve at *F*. At this point, the corrosion rate (current

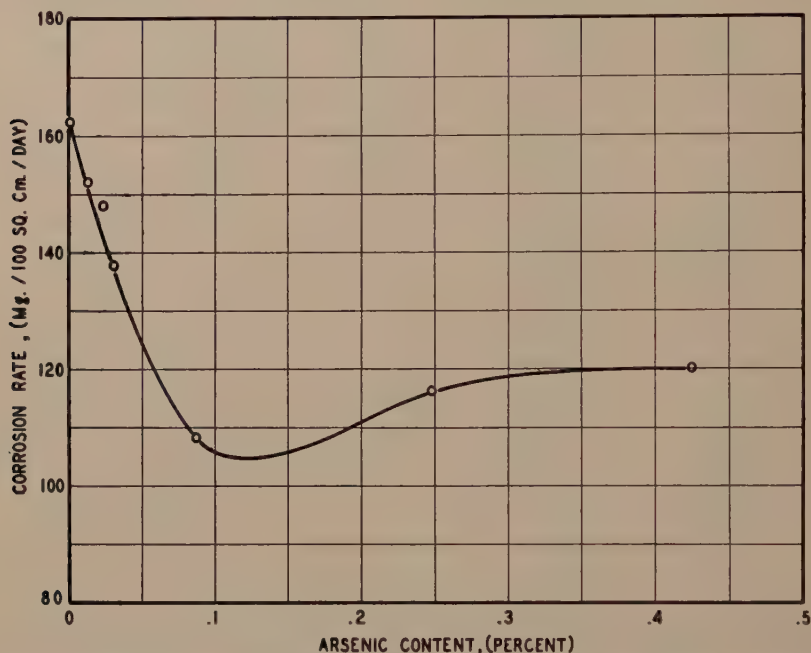


FIG. 16.—CORROSION RATE IN AERATED 4 PER CENT SODIUM CHLORIDE SOLUTIONS AS FUNCTION OF ARSENIC CONTENT OF BRASS.

rithm of the current density and the potential, it follows according to accepted theory¹⁷ that the increase in potential is due to a decreased overvoltage. Here it is necessary to point out that the overvoltage of the brass itself is not changed, but rather that the overvoltage of the brass filmed with arsenic is lowered. A third case, which concerns immersion of arsenical brasses in sodium chloride solutions, may be discussed with the aid of Fig. 17. The presence of zinc in solid solution in the copper makes the metal more electronegative (curves *C* to *A*). Curve *D* represents the dependence of potential on current density according to the oxygen reaction (Eq. *E*). At zero current density, the potential is that of a reversible oxygen electrode. From zero to the intercept *E*, the current density de-

pendence) is independent of potential but dependent on the rate of diffusion of oxygen to the interface. With the formation of an arsenical film on alpha brass the slope of the anode polarization curve becomes steeper, and its intersection with the oxygen curve approximates that of pure copper. The control of the corrosion, therefore, has been changed from one of diffusion to one of overvoltage by means of the formation of the arsenical film.

The reasons for the variations of potential immediately after immersion are not important to the main thesis of this paper. They depend entirely on the relative initial rates of the cathode and anode reactions.⁴

The effect of the arsenical film on the rate of corrosion is different in each of the

three previously mentioned cases. In case 1, the formation of the arsenical film lowers the potential of the brass to a value approximating that of plain copper. The corrosion of copper is due to the reduction of cupric to cuprous ion at the cathode, while the corrosion of plain brass is due to this reduction as well as to the reduction of cuprous ion to copper. Thus, the lowered potential of arsenical brass permits corrosion to occur in a manner equivalent to that of pure copper in air-free cupric chloride solutions.

The increased rate of corrosion of plain brass over arsenical brass for the reduction of cupric to cuprous ions is primarily caused by the superposition of two cathode reactions, *A* and *B*. Reaction *A* is affected only slightly by such superposition. The slight increase may be partly explained by the continuous removal of cuprous ion through the deposition of metallic copper. The amount of cuprous chloride precipitated is considerably less during the corrosion of plain brass than during the corrosion of arsenical brass, since the cuprous ion is now reacting to form copper. The decrease in precipitate permits an increase in the rate of diffusion of cupric ion to the interface. A second factor that serves to increase the rate of reaction *A* is the increase in anode area brought about by the deposition of copper. If the cathode reaction is simply the reduction of cupric to cuprous ion, the anode area is relatively small, and at no time does it occupy the entire specimen area.²¹ If copper covers the entire surface, it increases the effective anode area. In solutions containing oxygen, oxide may act as the cathode or as an insulating field, and it can continuously reform, whereas in air-free solutions the absence of oxygen prevents such re-formation. In other words, the copper that deposits in air-free solutions acts as cathode and subsequently a large part of the brass surface becomes the anode, since it is now free of oxide film. This conclusion is sub-

stantiated in that the rate of reduction of cupric to cuprous ions is the same for both arsenical and plain brass in aerated cupric chloride solutions. The rate of corrosion

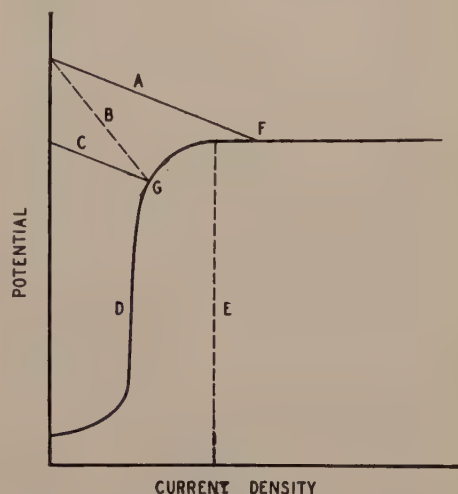


FIG. 17.—POLARIZATION CURVES IN AERATED SALT SOLUTION.

A, *B* and *C* are anode polarization curves, and *D* is the cathode polarization curve.

calculated from the actual specimen area should increase even though the rate as calculated from the actual anode area remains unchanged, for the anode area has increased. For electropositive metals (copper and brass), Müller²¹ estimates that the anode area occupies only about 1 per cent of the metal surface. Therefore, an increase of the anode area to 2 per cent doubles the effective corrosion rate of the brass. With present experimental techniques, the extent of the effective anode area cannot be determined, yet its importance as a factor in the actual rate of corrosion per unit area cannot be overlooked.

The aeration of the cupric chloride solutions does not affect the fundamental mechanism delineated above. The air serves to oxidize some of the cuprous ion to cupric and, in the absence of sufficient acid, to precipitate basic cupric chloride. The effect on the corrosion is to decrease the rate of deposition of copper and not

appreciably alter the rate of reduction of cupric to cuprous ion. When acid is present, basic cupric chloride does not precipitate and the rate of reduction of cupric to cuprous ion is markedly augmented by the resulting increase in concentration of cupric ion.

The second case concerns the rate of corrosion in hydrochloric acid solutions. The arsenic film decreases the overvoltage and increases the rate of corrosion of the brass. Such an effect of arsenic on overvoltage is in accord with Masing's measurements. It cannot, however, influence dezincification in cupric chloride solutions, for hydrogen is not evolved therein.

In aerated sodium chloride solutions (case 3), the increase in potential of brass caused by the arsenic changes the control from one of diffusion to one of overvoltage and hence decreases the corrosion rate. The corrosion rate is not quite reduced to that of copper in these solutions.

The results obtained in this study permit us to regard copper and arsenical alpha brass as electrochemically similar alloys, except in solutions in which a gas is evolved at the cathode. This similarity is due primarily to the formation of a film during the corrosion of arsenical brass. The film increases the effective potential by increasing the anode polarization. The effect of more positive potential on the corrosion rate is dependent on the nature of the corrodent. Since copper cannot reduce cuprous ion to copper, it may be concluded from the electrochemical similarity between copper and arsenical brass that copper will not redeposit during the corrosion of the latter alloy. This is sufficient explanation for the inhibition of dezincification by arsenic.

CONCLUSIONS

The corrosion of alpha brass occurs by the solution of the alloy as an entity. Dezincification occurs by reduction of the

cupric ion to cuprous ion followed by the reduction of the latter ion to metallic copper. During corrosion of arsenical brass, the arsenic enters solution as the trivalent ion and subsequently redeposits upon the brass surface. The arsenical film increases the effective potential practically to that of copper and prevents the deposition of copper. The beneficial effect²² of antimony and phosphorus may be explained analogously to that of arsenic, for films are formed during the corrosion of alpha brasses containing both of these elements. This explanation does not require an anode film as postulated by Fink and Evans, nor does it affirm Masing's point of view that the inhibition is due to the lowered hydro- gen overvoltage.

ACKNOWLEDGMENT

The present work has been made possible by a research grant from the Revere Copper and Brass Company.

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DISCUSSION

(E. A. Anderson *presiding*)

A. W. TRACY,* Waterbury, Conn.—In one of the curves the authors show that about 0.024 per cent arsenic changed the potential of brass to about the potential of copper. Should we assume that a lower arsenic content would not prevent the redeposition of copper?

W. A. WESLEY,† Bayonne, N. J.—There is an opportunity for confusion of the reader because in part of the paper (Fig. 13) the authors demonstrate an increase in corrosion rate accompanying an increasing potential, whereas in Fig. 17 a decrease in corrosion rate is shown accompanying an increase in potential. It would be well if the authors were to make the reasons for this difference a little clearer. The two different relationships can be illustrated by considering (1) an aerated sodium chloride solution and (2) a hydrochloric acid solution free from air. Typical anode and cathode polarization curves for case 1 are represented in Fig. 17, where the corrosion rate of copper alloy *A* is equivalent to the current at intersection *F*. If we take another copper alloy *C*, with a more noble potential, whose polarization curves intersect at point *G*, the corrosion rate of *C* is lower than that of *A* while the potential of alloy *C* is higher (more noble) than that of *A*.

Turning to the second case, the anode polarization curves for two alloys *D* and *E* in anaerobic hydrochloric acid solution can be considered to be closely alike as in Fig. 18 whereas the cathode curves may be quite far apart, since they depend upon the hydrogen overvoltage of the alloy surfaces, that of alloy *D* being smaller than that of alloy *E*. In this case alloy *E* corrodes more slowly than alloy *D* but its potential is lower (less noble) than that of *D*.

J. R. FREEMAN,‡ Waterbury Conn.—Were studies made of the specimens to determine whether intercrystalline corrosion was apparent in the surface of the specimens, or whether the corrosion was only general in character? Further, if intercrystalline corrosion was

noted, was there any difference in the degree of intercrystalline attack in specimens of different chemical compositions? What would be the effect of the presence of tin on all the various reactions discussed in the paper?

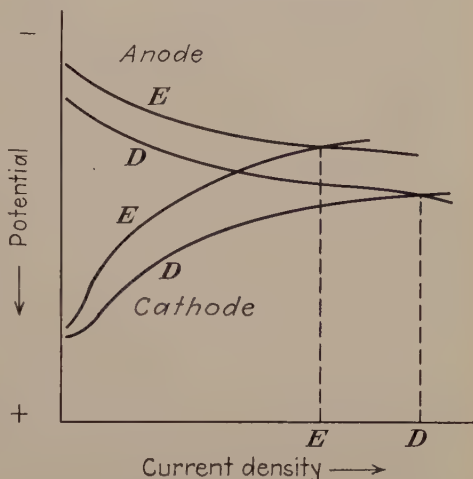


FIG. 18.—POLARIZATION CURVES IN AIR-FREE HYDROCHLORIC ACID (SCHEMATIC).

D. K. CRAMPTON* AND H. L. BURGHOFF,† Waterbury, Conn.—Inasmuch as the authors' experiments were of comparatively short duration, it is hardly to be expected that any great degree of corrosion would be encountered. However, such intercrystalline corrosion of arsenic-bearing Admiralty brass has been observed by the present writers for more normal conditions of exposure, both in laboratory test samples and in tubes subjected to actual service.

Fig. 19 shows the phenomenon in an annealed-strip tensile specimen of the alloy, which had been exposed for 100 days at 60°C. in dilute synthetic sea water in a laboratory test. It is to be noted that the synthetic sea water is not an unduly aggressive medium for laboratory corrosion testing and is representative of many waters that come into contact with metals in actual service.

Intercrystalline corrosion is also apparent in Fig. 20, which is a photomicrograph of the structure of an arsenic-bearing Admiralty condenser tube from actual service. The

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cooling medium was sea water, which passed inside the tube. The tube wall was thinned at the inner surface by intercrystalline corrosion, which was so serious that failure resulted.

whereas most of the observed data are explicable by an electrochemical approach to alloy corrosion.

When no replating occurs, studies on the

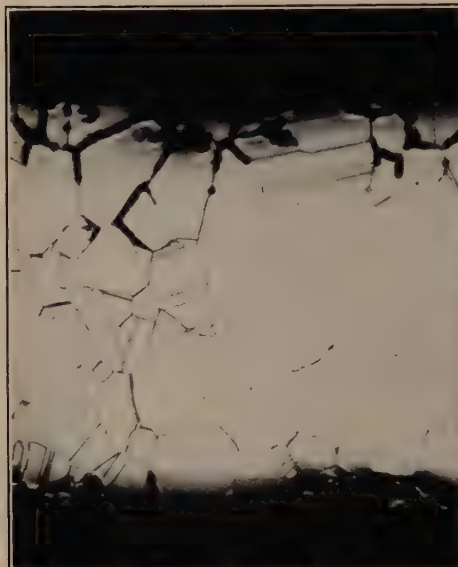


FIG. 19.—INTERCRYSTALLINE CORROSION IN LABORATORY TEST SPECIMEN. LONGITUDINAL CROSS SECTION. $\times 75$.

Analysis: 71.34 per cent Cu; 1.06 Sn; 0.11 As; <0.05 Pb; 27.49 Zn (by difference).

W. LYNES,* Rome, N. Y.—Was any information developed as to the solubility limit of arsenic in 70-30 brass?

C. S. SMITH,†—What is the maximum solubility of arsenic in alpha brass?

R. LANDAU,‡ New York, N. Y.—The authors have presented additional evidence against the concept of selective solution of one alloy constituent and instead have focused attention on the electrochemical factors involved, with fruitful results. This idea of selective solution was first widely disseminated by Tammann and his school in conjunction with their theory of resistance limits in alloy corrosion, with considerable confusion in the interpretation of the effect of changing corroding conditions. No one has ever conclusively demonstrated that such a phenomenon exists,

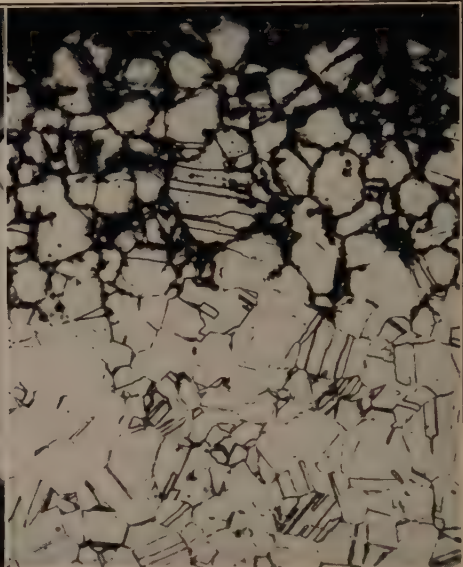


FIG. 20.—INTERCRYSTALLINE CORROSION IN CONDENSER TUBE THAT FAILED IN SERVICE.

Analysis: 70.20 per cent Cu; 1.07 Sn; 0.05 As; 0.02 Pb; 0.01 Fe; 28.65 Zn (by difference).

ratio of the metal ions found in solution (Mg-Cd, Cu-Ni, Ni-Mo, stainless steel) show that even for alloys where a low corrosion rate exists, this ratio is the same as in the metal. Selective solution therefore is unlikely. It would have been instructive if the authors had measured the zinc ion and copper ion concentrations in solution for cases where there was no replating.

Graf's X-ray studies on the corrosion of copper-gold alloys showed that the gold found on the surface came by replating from solution, but was not protective. On the *resistant* high-gold end of the series, however, his technique could detect no gold on the surface. It would be very valuable if the present authors' radioactive tracer studies and electron diffraction methods could be applied to such examples to determine whether any replating occurs (which should give a sharp boundary between the plate and the underlying metal, as Graf found) and whether it protects the alloys, or whether there is really selective solution (which should

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give an irregular and more or less gradual noble metal gradient from the surface to the bulk metal).

The authors show that arsenic plates out on brass, making the potential more noble, with protective effects. However, this plating must occur at the local *cathodes*, and if arsenic is substantially as good a conductor as the original alloy cathode, it would be difficult to understand why a more *positive* potential, or an inhibition of the corrosion rate should be observed. In other words, the film should grow in thickness but not in area. Thus, in my own work with Ni-Mn alloys in air-free acid it was found that Ni replated on the Mn, but the corrosion rate after 5 min. (no replating) and after 2 hr. (a heavy coat of redeposited nickel) was essentially the same. In some cases, however, the authors apparently have observed an increase in the effective film area, which leads to a higher IR drop in the pores of the film. The behavior of the nickel, therefore, is different from that of the arsenic.

In aerated sodium chloride solution, the formation of arsenious oxide with a swelling of the lattice might explain such an observed decrease in the anode area as contrasted with the nickel on Ni-Mn (where oxide formation was impossible). It may be that the fact that the authors found no effect of arsenic in NaCl corrosion after a certain percentage of arsenic is related to this. After an initial swelling period further expansion is impossible, and the film thickens without spreading. However, the same facts may be explained by the greater corrosion resistance of arsenic compared to the "oxide" films on plain brass, so that over a given time interval fewer film breakdowns occur on an arsenic-plated sample than on plain brass, with effectively a smaller anode area on the arsenical brasses. There may also be plugging up of the pores by insoluble corrosion products.

In air-free and aerated cupric chloride solutions, the explanation may lie in the relative effect of the copper and arsenic on the anode area as discussed by the authors. In acid solutions it appears to be the overvoltage effect of arsenic, and not the area, that predominates. It would be worth while to have the authors' opinion on these points and also on the question of the relative conductivity of As_2O_3 , arsenic, and the "oxide" films on copper and brass.

If a poorly conducting film resulted from arsenic replating, there should be found a low corrosion rate, but a more negative potential, contrary to the observed behavior.

J. H. HOLLOMON AND J. WULFF (authors' reply).—In answer to Mr. Tracy, we find that brasses containing 0.014 per cent arsenic tend to dezincify in all solutions we studied. Both arsenic and copper redeposit upon this alloy whereas only arsenic redeposits upon the alloy containing 0.024 per cent arsenic in most solutions. In many concentrated air-free cupric chloride solutions copper will deposit to some extent on all arsenical brasses. An alloy containing 0.024 per cent arsenic will prevent dezincification in aerated sodium chloride, yet the alloy containing 0.084 per cent arsenic exhibits the minimum corrosion rate, as shown in Fig. 16.

Dr. Wesley has brought up an important point concerning the electrochemical principles of corrosion. In general we agree with his remarks, but it is necessary to point out that in Fig. 17 curve *A* refers to alpha brass, *B* to a filmed alpha brass and *C* to pure copper. The effect of the film is to change the slope of curve *A* to that of *B* but not to change the reversible electrode potential. Dr. Wesley seems also to have overlooked this point in his Fig. 18.

The question brought up by Mr. Freeman as well as Dr. Crampton and Dr. Burghoff concerning intercrystalline corrosion is of great interest to all fabricators and users of brass condenser tubes. We did not observe such attack in any of the samples employed. Yet, as illustrated by Crampton and Burghoff, it may in time occur in arsenical alloys of alpha brass of different composition or of different thermal or mechanical prehistory. In any case, a chemical or stress concentration at the grain boundaries is a prerequisite for intergranular corrosion.

There are no published data on the ternary system, copper-zinc-arsenic. We tried to measure the solubility of arsenic in alpha brass by the X-ray back-reflection focusing technique. We were unsuccessful because slight changes in zinc content from one alloy to another masked the effect of changes in the arsenic content. There was ample indication, however, that 0.428 per cent arsenic does not

exceed the solubility limit. We trust this answers Mr. Lynes and Dr. Smith.

Mr. Landau's remarks on redeposition during the corrosion process are of great interest to all interested in an interpretation of corrosion phenomena. Differences in our observations of brass in contrast to those of Mr. Landau on nickel-manganese alloys are probably due to the different metallic nature of the arsenic as compared with nickel. Arsenic is a much poorer

conductor than nickel. Furthermore, in aerated solutions the arsenic is always filmed with arsenious oxide. We believe that the cause of the increased resistance with time of the filmed brass is due to the "plugging up" of the pores by insoluble corrosion products. In aerated solutions the precipitate filling is a basic cupric chloride and in air-free solutions cuprous chloride. In other words, the arsenical film also serves as an anchor for the insoluble precipitates.

Rates of High-temperature Oxidation of Dilute Copper Alloys

By F. N. RHINES,* MEMBER, W. A. JOHNSON† AND W. A. ANDERSON,‡ JUNIOR MEMBERS A.I.M.E.

(Philadelphia Meeting, October 1941)

THE rate of the high-temperature oxidation of pure copper has been measured repeatedly by numerous investigators. It appears to be generally agreed: (1) that at constant temperature, after the initial stages of oxidation have been passed and the scale has attained a substantial depth, the film thickness increases in proportion to the square root of the time of oxidation; and (2) that for any given period of oxidation the logarithm of the square of the film thickness is proportional to the reciprocal of the absolute temperature of oxidation.¹ These relationships are explained upon the basis that the rate of diffusion of copper to the external surface of the film is the controlling factor in establishing the rate of growth. Extensive studies have been devoted also to the mechanism and rates of the early stages of oxidation. There is thus available a reasonably well established theory of the oxidation of pure copper upon which to construct an explanation of the more complex oxidation of copper alloys.

Few general principles have as yet emerged from the chaos of observations that have been reported in the field of the oxidation of alloys.² It is evident, however, that the copper alloys may be divided into two main groups, whose oxidation characteristics are distinguish-

able. The first group, composed of the alloys with the noble metals, forms substantially pure copper oxide scales; the alloying element is concentrated within the residual metal, and sometimes particles of almost pure noble metal are found in the scales completely surrounded by copper oxide. In the second group, composed of the alloys of copper with the baser metals, the alloying element appears as an oxide in the scale, often in greater concentration than in the alloy itself and sometimes to the exclusion of copper oxide. The oxide scales of the latter class have been found to be made up of one, two, and sometimes more distinguishable layers of which the innermost is often metallic in character, composed of particles of the oxide of the alloying element embedded in essentially pure copper and known as the subscale or zone of internal oxidation.

The need for a thorough quantitative study of these modes of oxidation is evident. Since it is apparent that several mechanisms must be cooperating to produce the complex oxide scales found on copper alloys, the analysis of the process into its several simple operations should prove instructive. Fortunately, it is possible experimentally to produce internal oxidation in the absence of an external scale; this permits the isolation and intensive study of one of the steps in the oxidation process.

In the present research the rates of internal oxidation of an extensive series of dilute solid solution alloys of copper have been measured and a theory has been developed to predict the observed

Manuscript received at the office of the Institute June 12, 1941. Issued as T.P. 1368 in METALS TECHNOLOGY, October 1941.

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‡ Research Assistant, Metals Research Laboratory, Carnegie Institute of Technology.

¹ References are at the end of the paper.

rates. A beginning has been made, also, in the study of the rates of the combined internal and external oxidation of this series of alloys and in the development of a theory of combined oxidation. The results of a preliminary investigation of the structural characteristics of internal oxidation in these alloys have been published previously.³

RATES OF SIMPLE INTERNAL OXIDATION OF BINARY ALLOYS

The alloys used are listed in Table 1, and the details of their preparation were described in the paper just mentioned.³ In order to induce internal oxidation without formation of a surface scale, the samples were embedded in a mixture of equal parts of cuprous oxide and copper metal powders, enclosed in a tight iron capsule, and held at an elevated temperature (600°, 750°, 875°, or 1000°C.) for a measured interval of time (1 to 192 hr.). This treatment is the equivalent of heating the alloys in an atmosphere having a partial pressure of oxygen equal to the decomposition pressure of cuprous oxide and should very nearly maintain the saturation concentration of oxygen in the surface of the metal without permitting the formation of a primary cuprous oxide scale.

Heat-treatments were carried out in an automatically controlled electric muffle furnace with a maximum temperature variation of $\pm 5^\circ\text{C}$. Care was taken to utilize only the central portion of the muffle where the temperature gradient was least.

Samples approximately $\frac{1}{2}$ by $\frac{1}{2}$ by $\frac{1}{4}$ in. were cut from cold-rolled plate (reduced 75 per cent directly from the cast state); immediately before oxidation the broad surfaces were cleaned and smoothed on fine metallographic emery paper. After oxidation the samples were sectioned perpendicular to the broad face, polished, and etched. The depth of

oxidation was measured at 10 points in the cross section, with a sensitive micro-comparator. In all, somewhat more than a thousand samples were measured in this way.

Because of the voluminous nature of these data, it is impractical to reproduce the individual measurements here. Instead, the values have been averaged and incorporated in the constants of an expression embodying the familiar parabolic law and the log penetration squared versus reciprocal of the absolute temperature relationship; namely,

$$\log \frac{X^2}{t} = \frac{a}{T} + b \quad [1]$$

where X is the depth of penetration in centimeters in a time of t seconds, T is the absolute temperature, and a and b are the constants, which are unique for each alloy (Table 1).

This treatment demands a proof of the validity of equation 1, which is identical in form with the relationship governing the growth of an external scale on pure copper. If it is valid for the present case, the square of the depth of internal oxidation at constant temperature should be a linear function of the time. In every case examined this condition was found to hold; a few typical examples are plotted in Fig. 1. In addition, it is required that the logarithm of the depth of oxidation squared should be a linear function of the reciprocal of the absolute temperature for any fixed time interval. Over a temperature range from 750° to 1000°C., and except in a few special cases that will be discussed presently, this condition was very precisely met (Fig. 2). At 600°C. large deviations occur.

The facts are now at hand for the postulation and testing of a theory of internal oxidation. Let it be assumed that the diagram of Fig. 3 represents the distribution of dissolved oxygen and dissolved alloying metal (solute) at some

TABLE I.—Rates of Oxidation of Copper Alloys

Solute Metal	Concentration, Weight Per Cent	Constants of the Formula $\log \frac{X^2}{t}$ $= \frac{a}{T} + b$ for Subscale Formed Alone		Constants of the Formula $\log \frac{X^2 CM}{t}$ $= \frac{a'}{T} + b'$ for Subscale Formed Alone		Values of $\frac{X^2}{t}$ for Subscale Formed Alone at 600°C.	Constants of the Formula $\log \frac{S^2}{t} = \frac{c}{T} + d$ for Subscale Formed under an External Scale		Values of $\frac{S^2}{t}$ for Subscale Formed under an External Scale at 600°C.	External Scale	
		a	b	a'	b'		c	d		Values of $\frac{E_2}{t}$	Temperature of Oxidation, Deg. C.
Al	0.03	-12110	4.110	-10350	1.035	2.45×10^{-12}	-11890	3.614	2.02×10^{-10}	4.25×10^{-9}	750
Al	0.06	-11580	3.261	-10350	1.035		-11680	3.185	1.05×10^{-10}		
Al	0.08	-11540	3.142	-10350	1.035		-11710	3.053	1.46×10^{-10}		
Al	0.17	-12160	3.142	-10350	1.035	6.52×10^{-11}	-12020	2.912	8.51×10^{-11}	$\begin{Bmatrix} 2.54 \times 10^{-9} \\ 3.90 \times 10^{-9} \\ 6.35 \times 10^{-9} \\ 3.16 \times 10^{-8} \\ 1.09 \times 10^{-7} \end{Bmatrix}$	$\begin{Bmatrix} 750 \\ 875 \\ 750 \\ 875 \\ 1000 \end{Bmatrix}$
Al	0.45	-11970	2.983	-10350	1.035		-10800	1.215			
Al	0.72	-12140	2.753	-10350	1.035		-12140	2.015			
B	0.05 ^a	-10420	2.882	-10400	1.582	5.76×10^{-11}	-10420	2.762		1.13×10^{-7}	1000
Ba	0.10	-13480	5.228	-13700	4.582	1.82×10^{-10}	-13480	4.248	7.10×10^{-11}		
Be	0.018	-11150	3.330	-10420	0.542	2.42×10^{-10}	-11150	3.492	2.96×10^{-10}	1.72×10^{-7}	1000
Be	0.054	-14290	4.830	-10420	0.542	6.13×10^{-11}	-14290	4.487	1.39×10^{-10}		
Be	0.101	-11080	2.652	-10420	0.542	7.74×10^{-11}	-11080	2.572	2.44×10^{-11}		
Ca	0.01 ^a	-10080	2.121	-11150	0.974	5.18×10^{-10}	-10080	1.955	2.26×10^{-10}	1.61×10^{-7}	1000
Cb	0.04	-10250	2.742	-10210	1.328	8.39×10^{-11}	-10250	2.681	3.20×10^{-10}		
Cd	0.28										
Ce	0.01 ^a	-10870	2.984	-10880	1.009	5.05×10^{-11}	-10870	2.984	1.28×10^{-10}	1.83×10^{-7}	1000
Co	0.14	-10500	2.842	-11750	2.932	7.10×10^{-13}	-10500	2.812	2.68×10^{-10}	1.31×10^{-7}	1000
Cr	0.08	-11910	3.910	-11450	2.557	2.45×10^{-12}	-11910	3.824	1.45×10^{-12}	1.79×10^{-7}	1000
Fe	0.037	-11220	3.944	-10260	1.594						
Fe	0.10	-10390	2.509	-10260	1.594	4.19×10^{-12}	-10390	2.620	1.75×10^{-12}	2.07×10^{-7}	1000
Fe	0.56	-10730	2.393	-10260	1.594	9.08×10^{-11}	-10730	2.072		1.40×10^{-7}	1000
Fe	1.52	-10630	1.885	-10260	1.594	3.68×10^{-11}	-10630	1.533		1.11×10^{-7}	1000
Fe	2.65	-10310	1.288	-10260	1.594	4.70×10^{-12}	-10310	0.878		1.35×10^{-7}	1000
Ga	0.03	-15880	7.357	-15930	5.885		-15880	7.135	4.80×10^{-10}		
Ge	0.02 ^a	-10210	1.996	-11470	1.543		-10210	1.790		1.59×10^{-7}	1000
In	0.25	-11300	3.376	-10720	2.206	3.93×10^{-11}	-11300	3.274	1.69×10^{-10}	1.78×10^{-7}	1000
Li	0.02	-10330	2.094	-11450	1.290	6.13×10^{-11}	-10330	2.011	1.07×10^{-10}		
Mg	0.10 ^a	-11830	3.453	-11130	1.773	4.24×10^{-11}	-11830	3.362	1.05×10^{-10}	1.66×10^{-7}	1000
Mn	0.033	-10980	3.452	-10620	1.640	4.71×10^{-12}	-10710	2.765	2.59×10^{-11}		
Mn	0.084			-10620	1.640		-10610	2.708	1.16×10^{-10}		
Mn	0.22			-10620	1.640		-10840	2.316	6.16×10^{-11}		
Mn	0.42	-10470	1.778	-10620	1.640	6.12×10^{-12}	-10570	1.648	1.04×10^{-11}	4.46×10^{-8}	875
Mn	1.55	-10500	1.452	-10620	1.640	1.78×10^{-11}	-10570	1.186	3.27×10^{-11}		
Ni	0.115	-11110	3.695	-12840	2.306	1.20×10^{-10}	-11110	3.660	3.48×10^{-10}	2.74×10^{-7}	1000
Ni	5.00 ^a	-13710	4.032				-13710	3.510		1.78×10^{-7}	1000
P	0.03	-12050	3.835	-11870	2.142	3.62×10^{-11}	-12050	3.703			
P	0.07	-11700	3.274	-11870	2.142		-11700	2.955			
P	0.24	-11050	2.050	-11870	2.142	2.32×10^{-11}	-11050	1.749			
Pb	0.03 ^a	-10610	1.115	-11290	0.150					1.84×10^{-8}	1000
Si	0.045	-11320	3.275	-11110	1.660	1.48×10^{-10}	-10800	2.614	1.57×10^{-10}		
Si	0.076	-11110	2.790	-11110	1.660	1.73×10^{-10}	-10680	2.181	3.91×10^{-10}	2.21×10^{-9}	750
Si	0.103	-11010	2.481	-11110	1.660	2.79×10^{-10}	-10720	2.048	1.53×10^{-10}		
Si	0.180	-10310	1.723	-11110	1.660	3.38×10^{-11}	-10730	1.914	1.19×10^{-10}	$\begin{Bmatrix} 2.84 \times 10^{-9} \\ 3.41 \times 10^{-8} \\ 2.30 \times 10^{-9} \\ 1.77 \times 10^{-8} \end{Bmatrix}$	$\begin{Bmatrix} 750 \\ 875 \\ 750 \\ 875 \end{Bmatrix}$
Si	0.30	- 9725	0.919	-11110	1.660	6.12×10^{-11}	-10050	0.952	8.58×10^{-11}		
Si	0.59	- 9345	0.407	-11110	1.660	5.36×10^{-11}	- 8950	-0.331	8.16×10^{-11}		
Si	0.858	- 7785	-1.205	-11110	1.660	1.33×10^{-10}			9.24×10^{-11}		
Si	1.93	- 6570	-2.709	-11110	1.660	1.27×10^{-10}	- 7010	-2.667	7.37×10^{-11}		
Sn	0.31	-11820	3.665	-13550	4.521	3.21×10^{-11}	-11820	3.536	7.51×10^{-11}		
Sr	0.10 ^a	-11140	3.602	-13510	4.492		-11140	3.344		1.69×10^{-7}	1000
Ta	0.04	-10810	3.208	-10820	1.843	6.50×10^{-11}	-10810	3.000	1.69×10^{-10}		
Ti	0.05	-10430	3.010	-10220	2.849					2.25×10^{-7}	1000
V	0.09	-13000	4.633	-13200	3.767	2.45×10^{-10}	-13000	4.492	7.72×10^{-11}		
Zn	0.16	-10840	3.185	-12750	3.855		-12180	3.861	5.22×10^{-11}	1.80×10^{-7}	1000
Zn	0.21	-12180	4.049	-12750	3.855	2.12×10^{-10}	-11110	2.809	2.64×10^{-10}	1.73×10^{-7}	1000
Zr	0.16	-11110	2.955	-10430	1.511				3.91×10^{-11}		
Al + Be	0.049 + 0.003	-13600	4.534			3.30×10^{-10}	-12150	2.132	1.76×10^{-11}		
Al + Sn	0.06 + 5.43	-12150	1.976			9.51×10^{-11}					
Al + Zn	0.13 + 9.29	-10500	0.991			3.62×10^{-13}	-10500	0.510	2.81×10^{-11}		
Be + Sn	0.02 + 0.30	-13500	4.357			7.92×10^{-11}	-13500	3.703	2.67×10^{-11}		
Be + Sn	0.006 + 4.93	-12380	2.440			7.52×10^{-10}	-12380	2.555	5.22×10^{-13}		
Be + Zn	0.03 + 9.52	-11040	1.307			5.21×10^{-13}	-11040	1.046	1.76×10^{-13}		
Si + Sn	0.085 + 5.02	-12000	2.342			1.66×10^{-10}	-12000	2.300	2.45×10^{-12}		
Si + Zn	0.085 + 0.81	-11120	1.337			3.34×10^{-11}	-11200	1.140	2.45×10^{-12}		

^a Chemical analyses are not available for these alloys.^b All samples containing cadmium exhibited liquation. Values of $\frac{X^2}{t}$ are as follows: 600°C., 2.32×10^{-12} ; 750°C., 1.92×10^{-9} ; 875°C., 8.41×10^{-9} ; 1000°C., 1.10×10^{-7} . The value of $\frac{S^2}{t}$ at 1000°C. is 8.48×10^{-8} .

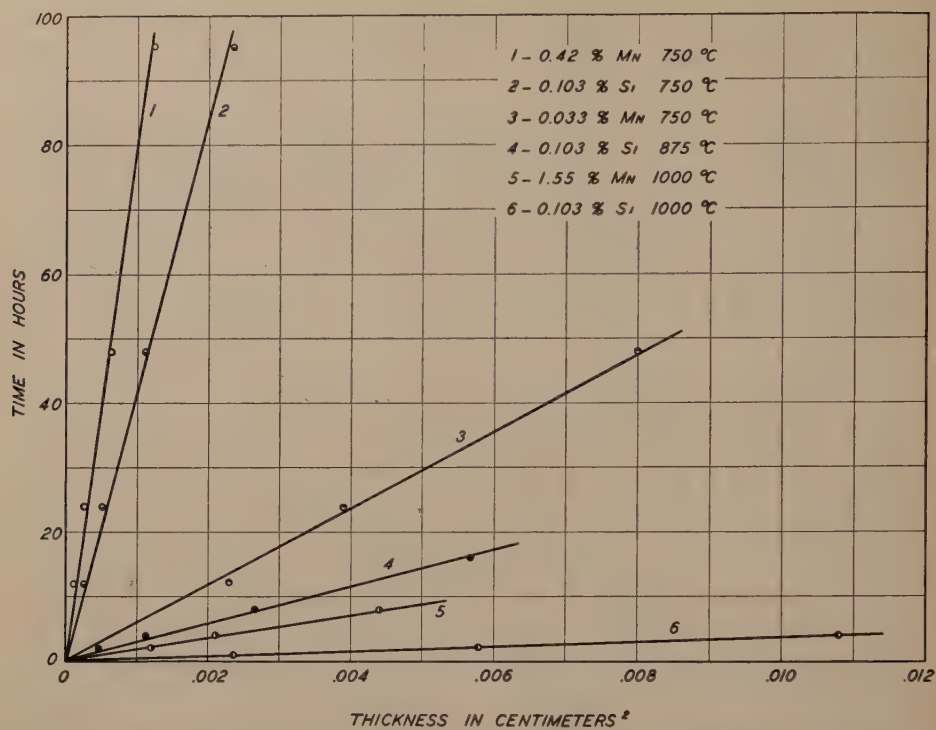


FIG. 1.—RELATIONSHIP BETWEEN TIME OF OXIDATION AND THICKNESS OF SUBSCALE, SHOWING THAT SIMPLE INTERNAL OXIDATION FOLLOWS PARABOLIC LAW.

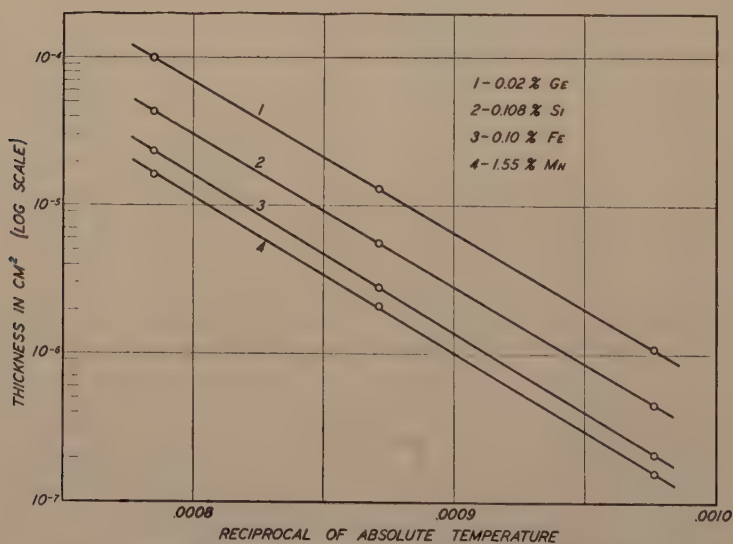


FIG. 2.—TEMPERATURE DEPENDENCE OF SIMPLE INTERNAL OXIDATION.

stage in the oxidation process. The oxygen is imagined to be supplied at the outside surface at a rate sufficient to maintain saturation of the surface copper with

has been measured.⁵ It appears reasonable to assume that the same rate would apply to the diffusion of oxygen across the subscale, except insofar as the precipitated

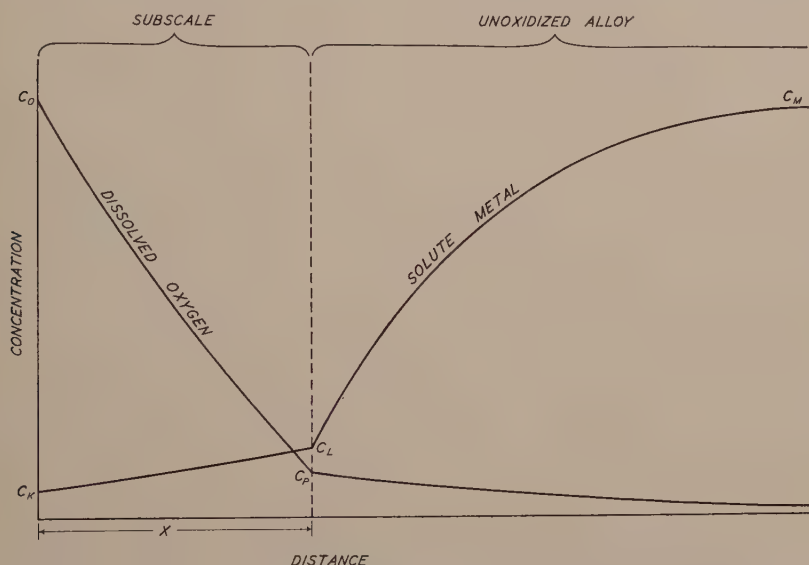


FIG. 3.—IDEAL DISTRIBUTION OF DISSOLVED OXYGEN AND SOLUTE ELEMENT DURING COURSE OF SIMPLE INTERNAL OXIDATION.

respect to oxygen, and diffusion inward occurs along the concentration gradient, $C_o - C_p$. At the interface between the subscale and the alloy, oxygen meets the solute and reacts to precipitate its oxide. Since the solute metal is removed from solution by this process, its concentration is reduced in the neighborhood of the subscale-alloy interface to some limiting value, C_L . This provides a concentration gradient in the alloy, and diffusion of the solute toward the interface occurs along the gradient $C_M - C_L$. As oxidation proceeds, the alloy becomes impoverished, thus reducing the rate of delivery of the solute metal, and the interface moves inward. The rate at which the interface will move inward—the rate of oxidation—will depend solely upon the relative rates of delivery of oxygen and solute metal at the interface and the quantity of each consumed in the reaction.

The rate of diffusion of oxygen in copper

oxide may obstruct the way. In dilute alloys the precipitate is sparsely distributed, and its effect will probably be negligible. Diffusion rates for several of the metals in copper have been measured also;⁶ there is no reason to suppose that these values should not apply to the present case. The relative quantities of oxygen and solute consumed in the reaction are dictated by the formula of the oxide.

By means of a derivation based upon Fick's law, but which will not be reproduced here,* it is possible to show that

* This and subsequent derivations have been placed on file at the offices of the American Documentation Institute as an Appendix to this paper. To obtain the Appendix, write to the American Documentation Institute, Office of Science Service, 2101 Constitution Ave., Washington, D. C., asking for Document No. 1588 and remitting 27¢ for copy in microfilm (read enlarged on machines now widely available), or 90¢ for photoprint (legible without optical aid).

this picture of the oxidation process at constant temperature can be expressed mathematically as follows:

$$\frac{X^2}{t} = \frac{2D_o(C_o - C_p)}{A\phi\left(\sqrt{\frac{K_1}{4D_o}}\right)} \sqrt{\frac{K_1}{\pi D_o}} \quad [2]$$

where:

$$A = 2 \frac{O}{M} \frac{(C_M - C_L)}{1 - \phi\left(\sqrt{\frac{K_1}{4D_M}}\right)} \sqrt{\frac{D_M}{\pi K_1}} e^{-\frac{K_1}{4D_M}} \\ + \frac{2C_p}{1 - \phi\left(\sqrt{\frac{K_1}{4D_o}}\right)} \sqrt{\frac{D_o}{\pi K_1}} e^{-\frac{K_1}{4D_o}} \\ + \frac{2(C_o - C_p)}{\phi\left(\sqrt{\frac{K_1}{4D_o}}\right)} \sqrt{\frac{D_o}{\pi K_1}} \left(1 - e^{-\frac{K_1}{4D_o}}\right) \\ + 2 \frac{O}{M} \frac{(C_L - C_K)}{\phi\left(\sqrt{\frac{K_1}{4D_M}}\right)} \sqrt{\frac{D_M}{\pi K_1}} \left(1 - e^{-\frac{K_1}{4D_M}}\right)$$

Here X is the depth of oxidation in centimeters in a time t seconds; D_o and D_M (centimeters squared per second) are the diffusion coefficients of oxygen and the alloying element respectively in copper; C_o and C_p are the maximum oxygen concentration (solubilities) in copper and the alloy, respectively; C_M is the original alloy concentration; C_L and C_K are the solute concentrations at the subscale interface and the outside surfaces, respectively, as indicated in Fig. 3; $\frac{O}{M}$ is the weight ratio of oxygen to metal in the oxide formed; ϕ is the value of the probability integral, and K_1 is a constant equal to $\frac{X^2}{t}$.*

The value of A in Eq. 2 is difficult to compute because of the complexity of the expression and the lack of experimental values of C_K , C_L and C_p . For the range of alloy compositions examined in the

present research a simple approximation, Eq. 3, may be substituted for Eq. 2. Advantage will be taken of the fact that C_K , C_L and C_p are very small values and may be assumed equal to zero.

$$\frac{X^2}{t} = \frac{2D_oC_o - 1.68 \frac{O}{M} C_M D_M}{\frac{O}{M} C_M + \frac{C_o}{3}} \quad [3]$$

Eq. 3 is accurate to within 1 per cent as long as the expression

$$\frac{D_oC_oM}{D_MC_MO}$$

is equal to, or greater than, five.

In order to test this expression, it is necessary only to fill out the terms from existing data, solve for X and compare the answer with the experimental results. Values of C_o , D_o and D_M will be selected*

TABLE 2.—Oxides Identified by X-ray

Diffraction Method		
(kappa)	Al ₂ O ₃	ZrO ₂
	SiO ₂	SnO ₂
	Cr ₂ O ₃	Pb ₃ O ₄
	Fe ₂ O ₃	ZnO
	TiO ₂	CoO

from the literature.^{4,5,6} (See Table 3.) To determine $\frac{O}{M}$ it is necessary to identify the oxide that is formed. Several of the oxides appearing in the alloys examined have been identified by X-ray diffraction methods,

* It should be pointed out that the values of C_o , D_o and D_M , taken from the literature, are subject to rather large errors. Several determinations of the solubility of oxygen in copper have been reported and the values differ by a ratio of 1 to 30. If the values of Phillips and Skinner⁷ or of Vogel and Pocher⁸ are employed here, instead of those of Rhines and Mathewson, the calculated rates of oxidation differ slightly from those here computed. The diffusion rate of oxygen in copper, D_o , was determined by the use of Rhines and Mathewson's solubility data and is thus subject to errors in these measurements, but the product C_oD_o is not so affected. Values of D_M taken from Rhines and Mehl's data are less dependable at low than at moderately high concentrations and within the low concentration range at present under consideration may be incorrect by a factor of as much as 50 per cent. Fortunately, large errors in D_M introduce but small errors in X .

* Although all of the concentration terms included here and in later equations refer to "true concentration," it is permissible to substitute "weight per cent" as long as all concentration terms are treated similarly.

and the results are reported in Table 2. Some of the diffraction patterns were obtained directly from the oxides in situ, while for others the copper was dissolved and the oxide concentrated and examined.

high. In the former case, since solid solubilities usually increase with temperature, it is to be expected that the C_L value and hence the error in the calculated rate of oxidation would increase with rising tem-

TABLE 3.—Comparison of Calculated with Observed Rates of Internal Oxidation

Solute	C_M , Weight Per Cent	T , Deg. C.	C_o , Weight Per Cent	$D_o \times 10^{-8}$	$D_M \times 10^{-10}$	$\frac{O}{M}$	Depth of Oxidation in 100 Hr., Cm.	
							Calculated	Observed
Al	0.03	750	0.0085	5	1.5	0.891	0.101	0.100
Al	0.03	875	0.0097	63	10.5	0.891	0.381	0.366
Al	0.03	1000	0.0117	480	50	0.891	1.145	1.212
Be	0.018	750	0.0085	5	2.5	1.771	0.093	0.103
Be	0.018	875	0.0097	63	13	1.771	0.353	0.399
Be	0.018	1000	0.0117	480	50	1.771	1.062	1.140
Si	0.045	750	0.0085	5	1.4	1.140	0.075	0.077
Si	0.045	875	0.0097	63	28	1.140	0.281	0.302
Si	0.045	1000	0.0117	480	340	1.140	0.859	0.935
Si	0.103	750	0.0085	5	1.4	1.140	0.049	0.045
Si	0.103	875	0.0097	63	28	1.140	0.186	0.172
Si	0.103	1000	0.0117	480	340	1.140	0.554	0.486
Si	0.180	750	0.0085	5	1.4	1.140	0.037	0.040
Si	0.180	875	0.0097	63	28	1.140	0.139	0.142
Si	0.180	1000	0.0117	480	340	1.140	0.417	0.396
Sn	0.31	750	0.0085	5	3.5	0.269	0.058	0.068
Sn	0.31	875	0.0097	63	44	0.269	0.219	0.237
Sn	0.31	1000	0.0117	480	340	0.269	0.665	0.940
Zn	0.21	750	0.0085	5	2	0.245	0.074	0.071
Zn	0.21	875	0.0097	63	20	0.245	0.278	0.312
Zn	0.21	1000	0.0117	480	120	0.245	0.852	1.041

Incorporating these data in Eq. 3, the values shown in Table 3 are obtained. Among some of the alloys the agreement between the calculated and observed rates is remarkably close, while in others rather large discrepancies occur. Where major deviations appear the calculated rate is usually slower. Large errors in this direction could be caused by using too large a value of C_o (with the corresponding D_o), by an incorrect identification of the oxide, or by an overestimation of the solute concentration gradient in the alloy during oxidation. If the product $C_o D_o$ is incorrect, all of the calculated rates should be in error; this was not found to be true. The effect of an error in C_o alone would be small but constant. It is very unlikely, too, that the oxides are wrongly identified. This leaves as a probable major source of error only the solute concentration gradient, which would be overestimated if C_L has a significant magnitude or if C_M is reported too

perature; there is a general trend of this nature to be seen among the data. Particularly is this true in the alloys containing tin and zinc, which form oxides that long have been suspected to be slightly soluble in copper. The initial alloy analyses (C_M) in most instances represent combined as well as dissolved solute. Thus, if some of the alloying element were oxidized before casting, the effective solute concentration would be lower than reported in the chemical analysis. Small quantities of oxide inclusions were seen in many of the alloys prior to oxidation, especially alloys containing aluminum, beryllium, silicon, and the other easily oxidizable metals. If, on this basis, it is assumed that the C_M values are high—that, for example, 0.008 per cent of silicon has been prematurely oxidized in the 0.045 per cent silicon alloy, leaving 0.037 per cent of unreacted silicon—and if this figure is substituted in Eq. 3, it will be found that the calculated and observed

rates are in close agreement. The same kind of correction can be successfully applied to the other alloys.

Upon the basis of this and additional similar evidence, it has been concluded that Eq. 2 provides a satisfactory quantitative description of the process of internal oxidation and that Eq. 3 is sufficiently accurate for practical purposes where it is desired simply to estimate the depth of internal oxidation under some specified set of conditions. Caution must, of course, be exercised in applying Eq. 3 to alloys containing elements that form less stable oxides (tin, indium, zinc, for instance).

It should be clearly understood that the foregoing applies to dilute alloys of copper, oxidized in an environment of cuprous oxide and examined only after oxidation has been proceeding for some time. There is reason to believe that the initial stages of internal oxidation involve complications that presently disappear, and that the whole mechanism is modified in the more concentrated alloys.

Eq. 3 provides a means of interpolation between the oxidation rates of the various alloy concentrations listed in Table 1 and, whether or not the D_M values are known, can be used in this way to calculate the depth of oxidation of an alloy under stated conditions of time and temperature. This equation is cumbersome, however, and for very short interpolations a much simpler relationship,

$$\log \frac{X^2 C_M}{t} = \frac{a'}{T} + b' \quad [4]$$

may prove convenient and sufficiently accurate. Values of a' and b' are listed in Table 1. In general these may be used only in the range from 0.1 to 1 per cent of the alloying element. Within this range the error is usually not more than 5 per cent.

Throughout the group of alloys examined, regular oxidation behavior was confined to the temperature range 750° to 1000°C. Alloys oxidized at 600°C. exhibited

very irregular behavior, their oxidation rates varying from five-thousandths to three times the expected rates. It was pointed out in the earlier publication³ that between 750° and 600°C. the mechanism of internal oxidation suffers a marked change. At the higher temperatures the oxide is precipitated generally throughout the copper crystals, while at lower temperatures the oxide appears largely or exclusively at the grain boundaries. In some cases the grain boundaries appear to be forced open by the large quantity of oxide, while in others the boundaries appear sound but the grains are largely or entirely enclosed in an envelope of the oxide. It is conceivable both that ruptured boundaries could admit oxygen more rapidly than by the usual diffusion route, thus increasing the rate of internal oxidation, and that an envelope of oxide about the copper grains could interfere with the normal passage of oxygen and thereby decrease the rate of oxidation. As yet no definite correlation between the structural types and deviations from regular oxidation behavior has been established. The further study of this subject will require the development of more suitable research techniques and must be deferred for the present. Measurements of the rates of internal oxidation at 600°C. are recorded in Table 1.

Departures from the regular oxidation behavior (Eq. 1) were noted also at the higher temperatures among the alloys containing lead, cadmium, and high phosphorus. In all of these instances there is micrographic evidence that a liquid phase was present during oxidation.

In short, it has been concluded that the rate of simple internal oxidation in copper alloys is satisfactorily described by Eq. 2 within a temperature range of 750° to 1000°C. as long as the alloy content remains low (within the alpha solid solution range, or at least within the copper-rich part of this range) and no liquid phases form. In alloys in which very stable oxides form the

rate of oxidation is described quite satisfactorily by the simpler Eq. 3. Below about 700°C., at and above temperatures where melting occurs and among the more con-

centrated alloys, the process of internal oxidation becomes more complex and the simple theory does not apply.

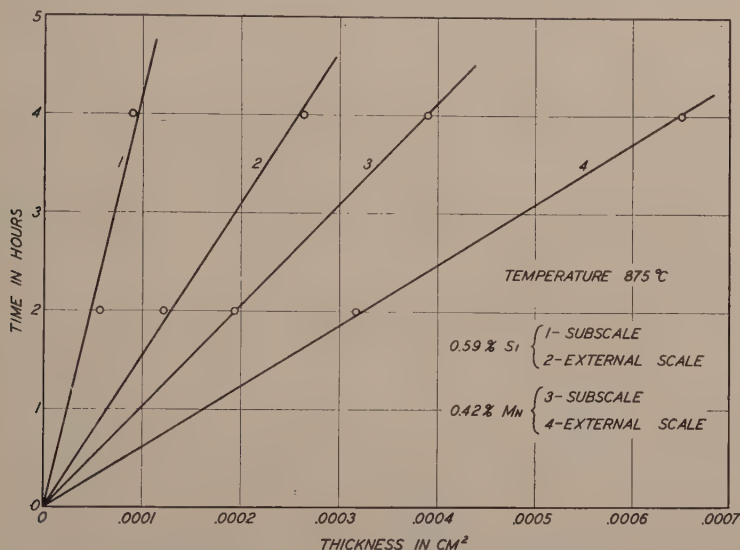


FIG. 4.—RELATIONSHIP BETWEEN TIME OF OXIDATION AND THICKNESS OF SURFACE AND SUBSCALES, SHOWING THAT PARABOLIC LAW IS OBEYED BY BOTH INTERNAL AND EXTERNAL OXIDATION WHEN THE TWO OCCUR CONCURRENTLY.

centrated alloys, the process of internal oxidation becomes more complex and the simple theory does not apply.

RATES OF INTERNAL OXIDATION IN PRESENCE OF EXTERNAL OXIDATION IN BINARY ALLOYS

As a second step in the analysis of the oxidation problem, the modifications that appear in the internal oxidation process when an external oxide film is forming concurrently have been briefly explored. Metallographic studies³ have failed to show any important difference in the structure of the subscale formed under an external oxide layer; there is, however, a diminution in the rate of growth.

Samples similar to those described in the preceding pages were oxidized at elevated temperatures (600°, 750°, 875°, and 1000°C.) in the air. In order to ensure adequate access to the air, the samples were

set on edge, well spaced on Sil-O-Cel bricks; they were heated in a slightly open electric muffle furnace. During cooling the external scale largely flaked off and was lost. In a

limited series of experiments the external scale was preserved in place by embedding the samples in Wood's metal before they had cooled to room temperature. Measurements of the thickness of the internal and external scales were made by the usual technique.

As before, the measurements have been averaged and assembled in the constants of the expression:

$$\log \frac{S^2}{t} = \frac{c}{T} + d \quad [5]$$

justification for which is taken from the evidence of Figs. 4 and 5. The values of the constants c and d for all of the alloys examined are recorded in Table 1.

Rate measurements were made over the complete temperature range only among the alloys containing aluminum, manganese, and silicon. All other alloys were studied at only two temperatures: 600° and

1000°C. Since the rates at 600°C. were found to be irregular, and therefore not suited for the calculation of c and d , it was necessary, among these alloys, to assume a

oxidation in the presence of an external scale, are parallel with those corresponding to internal oxidation in the same alloys oxidized without an external scale, c and a

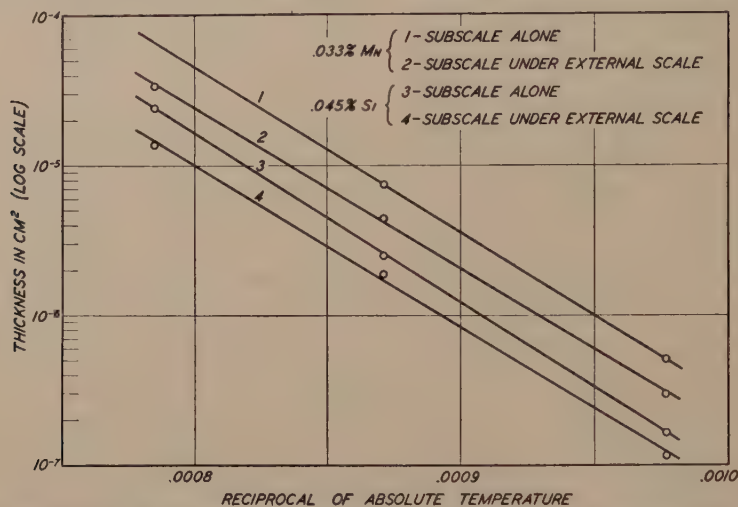


FIG. 5.—COMPARISON OF TEMPERATURE DEPENDENCE OF SIMPLE AND COMBINED INTERNAL AND EXTERNAL OXIDATION.

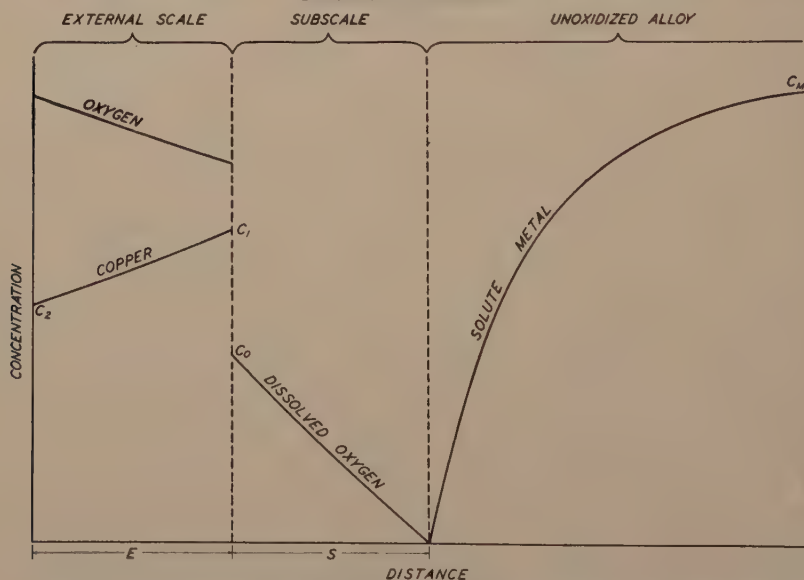


FIG. 6.—IDEAL DISTRIBUTION OF DIFFUSING ELEMENTS DURING COURSE OF COMBINED INTERNAL AND EXTERNAL OXIDATION.

value of c and to calculate d from the reading at 1000°C. The constant c , in fact, is the slope of a line such as 2 or 4 in Fig. 5. If these lines, corresponding to internal

should be identical constants. A comparison of these slopes in two alloys is presented in Fig. 5. While the curves of these pairs are not precisely parallel, an examination

of a larger group of cases led to the conclusion that c and a are approximately if not exactly identical, and the values reported in Table 1 have been computed accordingly. It follows that the constants c and d will reproduce experimental data at 1000°C. in all alloys listed, but will yield only approximations at other temperatures, except among the alloys containing aluminum, manganese, and silicon where experimental results will be reproduced at 750° and 875° as well as at 1000°C.

The mechanism of the process of combined internal and external oxidation is necessarily more complex than that of simple internal oxidation (Fig. 6). In order to derive a manageable mathematical expression of the process, it is advisable to introduce several simplifying assumptions: The concentration of oxygen in the unoxidized alloy and of the solute in the subscale will be taken to be zero; the presence of the oxide of the solute in the subscale and in the external scale will be presumed to have no effect upon the rate of the process; the presence of a surface layer of cupric oxide (always very thin) will be ignored; and the concentration gradients in the subscale and external scale will be assumed to be linear. Again the rates of delivery of oxygen and the solute at the alloy-subscale interface, together with the oxygen-metal ratio in the oxide precipitated, will be assumed to control the rate of growth of the subscale. The rate of growth of the external scale will be presumed to depend upon the rate of delivery of copper at the external surface, which is, in turn, controlled by the rate of diffusion of copper in cuprous oxide.

Upon this basis the following expressions for the rates of the concurrent growth of the subscale (Eq. 6) and the external scale (Eq. 7) have been derived:

$$\frac{S^2}{t} = \frac{2C_o D_o}{\alpha} \quad [6]$$

$$\frac{E^2}{t} = \frac{2(C_1 - C_2) D_{Cu}}{\beta} \quad [7]$$

where S and E are the depths of internal and external oxidation, respectively, in a time (t seconds). C_o and D_o are the maximum solubility and the diffusion coefficient of oxygen in copper, $(C_1 - C_2)$ is the concentration gradient of copper in a copper oxide scale (weight per cent), and D_{Cu} is the diffusion coefficient of copper in cuprous oxide. Alpha and beta represent the expressions:

$$\alpha = C_M \frac{O}{M} \left(1 + \delta \sqrt{\frac{K_E}{K_S}} \right) \left(1 + 1.68 \frac{D_M}{(\delta \sqrt{K_E} + \sqrt{K_S})^2} \right)$$

$$\beta = (1 - C_M) \delta + \alpha \frac{2Cu}{O} \sqrt{\frac{K_S}{K_E}}$$

where δ is the quotient of the product of the density of cuprous oxide and twice the atomic weight of copper over the product of the density of copper and the molecular weight of cuprous oxide, $\frac{2Cu}{O}$ represents the ratio of the atomic weights of copper and oxygen in cuprous oxide, the constant K_S is equal to $\frac{S^2}{t}$, the constant K_E is equal to $\frac{E^2}{t}$, and the other symbols retain their former significance.

In addition to the data necessary for solving Eq. 3, the solution of Eqs. 6 and 7 requires a knowledge of the value of the product $(C_1 - C_2) D_{Cu}$. This can be obtained from any one of several determinations of the rate of oxidation of pure copper,^{9,2} assuming that simple external oxidation obeys the expression:

$$\frac{Y^2 \delta}{2t} = \frac{(C_1 - C_2) D_{Cu}}{100}$$

where Y is the thickness of the oxide scale formed upon pure copper after t sec. of oxidation.

A direct solution of Eqs. 6 and 7 is mathematically impractical because of the manner in which K_S and K_E occur in the

equations. Instead, values of K_S and K_E must be assumed and the equation solved for first approximations of $\frac{S^2}{t}$ and $\frac{E^2}{t}$; revised values are then substituted for K_S and K_E to obtain second approximations,

the calculated subscale thickness is sometimes greater than the observed thickness when an external scale is forming concurrently is therefore to be associated with something present here for the first time, perhaps some error in describing the rate

TABLE 4.—Comparison of Calculated with Observed Rates of External and Internal Oxidation

Solute	C_M , Weight Per Cent	T , Deg. C.	$(C_1 - C_2)DCu$ $\times 10^{-7}$	Depth of External Oxide (E) or Subscale (S) in 100 Hr., Cm.				
				E		S		
				Calculated	Observed	Calculated	Observed	Corrected
Al	0.03	750	1.43	0.042	0.038	0.093	0.061	0.095
Al	0.45	750	1.43	0.041	0.047	0.017	0.0129	0.016
Al	0.45	875	14.0	0.126	0.107	0.072	0.097	0.076
Al	0.45	1000	87.4	0.314	0.247	0.235	0.260	0.249
Be	0.018	1000	87.4	0.323	0.249	1.031	0.923	1.053
Si	0.076	750	1.43	0.042	0.028	0.048	0.032	0.051
Si	0.18	750	1.43	0.041	0.032	0.028	0.028	0.030
Si	0.18	875	14.0	0.128	0.111	0.110	0.126	0.114
Si	0.59	750	1.43	0.040	0.029	0.012	0.0142	0.014
Si	0.59	875	14.0	0.124	0.080	0.048	0.068	0.052

and so on until values of K_S and K_E are found that yield identical values of $\frac{S^2}{t}$ and $\frac{E^2}{t}$.

These equations have been solved for a series of alloys; the results are shown in Table 4. Such basic data as are not listed in this table are taken from Table 3. While a general correspondence between the calculated and observed depths of oxidation is evident in Table 4, the agreement is far from perfect. It is noteworthy that the observed thickness of the external scale is generally less than the calculated thickness (usually about three-fourths) and that the observed thickness of the subscale is sometimes smaller and sometimes greater than the calculated thickness.

From the studies upon simple internal oxidation, Eq. 3, it is clear that the assumption made then and repeated here—i.e., that unoxidized solute is not present in the unoxidized alloy and that unoxidized solute is not present in the subscale—should always result in an underestimation of the thickness of the subscale. The result that

of growth of the external scale. The rates of growth of the two layers are, of course, interdependent. The most probable error in describing the rate of growth of the external scale is the assumption that the oxide of the solute in the external scale does not interfere with the diffusion of copper to the external surface. To test this, the rates of internal oxidation have been calculated from Eq. 6, taking for K_E the measured values of E^2/t ; the results are shown in Table 4 (column 8). The agreement between the calculated and measured subscale thickness is now for the most part a little closer, showing that the correction is of the right kind, but that some unidentified sources of error remain uncorrected.

Thus it is seen that Eq. 6 provides a reasonably accurate method for calculating the thickness of the subscale, and Eq. 7 a somewhat less precise method for calculating the thickness of the external scale. Once more it should be pointed out that these expressions apply to the oxidation of dilute alloys of copper oxidized in the air at temperatures between 750° and 1000°C.

At 600°C. the rate of growth of the subscale is again unpredictable, and measurements of $\frac{S^2}{t}$ at 600°C. have been listed separately in Table 1.

RATES OF INTERNAL OXIDATION OF TERNARY ALLOYS

Although no serious attempt has been made to investigate the rates of oxidation of the more complex alloys, the few data of this kind that have been collected serve to indicate in a general way the additional complications that will be encountered. This information, even though incomplete, should prove valuable, since few technical alloys are so pure as to behave as true binaries.

Metallographically,³ it has been found that when two solute elements are cooperating to form a subscale there are two distinguishable zones in the subscale. The outer zone is composed of two kinds of oxide particles precipitated together in a copper matrix, while the inner zone is composed of only one kind of oxide embedded in copper. This is the result of the more rapid oxidation of one of the solute elements. The greatest differences in these rates are observed when the two solute elements form oxides that differ greatly in their chemical stability; the more stable oxide (Al_2O_3 , BeO , and others) is deposited to a greater depth below the metal surface in a given time than is the less stable oxide (ZnO , SnO_2 , for instance). Even in extreme cases, however, the difference in the rate of oxidation is not very great, the more stable oxide perhaps forming a band one-fourth wider than the less stable one. Where the two solute elements form chemically similar oxides, the rates of oxidation are almost identical, producing what appears to be a single zone of subscale.

Realizing that the subscales in the complex alloys are not simple, it may prove helpful, nevertheless, simply to assume that a single zone of internal oxidation is

formed in these alloys. The direct calculation of the rate of growth of a multizone subscale introduces so many unknown quantities (such as the solute-oxygen equilibrium for each element involved) that the evaluation of any reasonable formula is impractical at present. If, instead, it is assumed that a single subscale is formed, involving the complete precipitation of all the oxidizable elements within its span, an expression describing the case is obtained by a simple modification of Eq. 2, or, for greater simplicity, Eq. 3. The terms involving the solute element are converted into a summation of similar terms involving each solute independently, thus:

$$\frac{W^2}{t} = \frac{2D_o C_o}{F} \left[1 + \frac{K}{12D_o} \right] \quad [8]$$

where

$$F = \frac{C_o}{2} + \frac{O}{M} C_M \left(1 + 1.68 \frac{D_M}{K} \right) + \frac{O}{N} C_N \left(1 + 1.68 \frac{D_N}{K} \right) + \text{etc.} \dots$$

Here W represents the thickness (average) of the subscale, and the subscripts M and N refer to the solute elements. It is to be noted that K_1 is the same in all terms and is equal to W^2/t .

The rate of subscale formation in a copper alloy containing 0.02 per cent Be plus 0.30 per cent Sn at 1000°C. has been calculated by the use of Eq. 8; the resulting value, 0.567 cm. in 100 hr., is to be compared with an observed extreme depth of oxidation of 0.468 cm. Since the observation of the subscale boundary in ternary alloys is somewhat uncertain and Eq. 8 is only an approximation, this degree of agreement may be considered acceptable.

Eight ternary alloys have been examined in this way; the measurements are listed in Table 1. It should be noted that in each entry the thickness of the subscale refers to the maximum thickness and not to the average.

DISCUSSION OF THE RESULTS

The theory of internal oxidation presented in the foregoing pages has been tested by comparison with experimental measurements and has been found to predict the measured rates of subscale formation within reasonably close limits. Thus the mechanism postulated is justified on the whole. It is to be anticipated that further advances toward a more complete understanding of this process must take the form of minor corrections to take account of the effects of secondary influences and to expand the range of alloys and conditions of oxidation that can be handled by the theory. The mechanism proposed for combined internal and external oxidation is somewhat less satisfactory. In this case corrections of a more important magnitude will be required to bring the theory into accord with the experimental findings. While it is not possible without further experimental work to ascertain the exact modifications that will be required to perfect the present theory, it will be profitable to examine the nature of the discrepancies between the observed and calculated rates of oxidation in Tables 3 and 4 in order to determine the kinds of modification that will be required.

Before proceeding with a discussion of the deviations from "regular behavior," it is appropriate that the precision of the experimental measurements should be examined. The values reported in Table 1 are averages, representing from ten to several hundred readings. For this reason they may be regarded as being more nearly correct than any one individual reading. Usually the differences among the individual readings are small, but occasionally differences as great as 50 per cent are encountered. Such errors seem to be characteristic of particular alloys and generally are not the result of inaccurate measurement alone. It should be noted also that the rates of oxidation are extremely sensitive

to the alloy content and that the analyses reported are subject to the usual analytical errors. Moreover, small quantities of impurities would have some, though probably a minor, influence upon the rates of oxidation. Small amounts of iron, seldom more than 0.01 per cent and usually much less, were present in most of the alloys. For these reasons it is impractical to designate a definite limit of error in this work. Experience has shown that the thickness readings can usually be duplicated within about 5 per cent.

It has been noted that in simple internal oxidation the calculated rate is often a little smaller than the observed rate, and that this difference becomes greater as the solute oxide involved becomes less stable; that is, the difference is greater in a copper-zinc alloy than in a copper-aluminum alloy. From this it may be concluded that the solute metal is only partly oxidized at the interface and that the degree to which oxidation proceeds depends upon the stability of the oxide formed. In other words, C_L has a significant value and should be taken into account in any precise calculation of the rate of oxidation. Moreover, if this is true, there will be for each solute a minimum concentration below which internal oxidation will not occur in a given atmosphere, and this concentration will be the larger the less the stability of the oxide. It is probably true also that the oxygen is not all consumed in the reaction and that there is similarly a minimum oxygen concentration (corresponding to a minimum oxygen pressure in the atmosphere) below which the internal oxidation of any specified alloy will not occur. This condition is written in Eq. 2, where it will be seen that if C_o becomes equal to or smaller than C_p , internal oxidation will cease.

In reality, the minimum solute and oxygen concentrations necessary to produce internal oxidation are probably considerably larger than the equilibrium values of C_L and C_P . A certain degree of super-

saturation with respect to one or both of these elements appears to be necessary before nuclei of the oxide will form. This is suggested by the observation that the oxide

the blocking effect of the solute oxide may be even more pronounced. Froelich² and others have reported a pronounced tendency for some of the solute oxides to

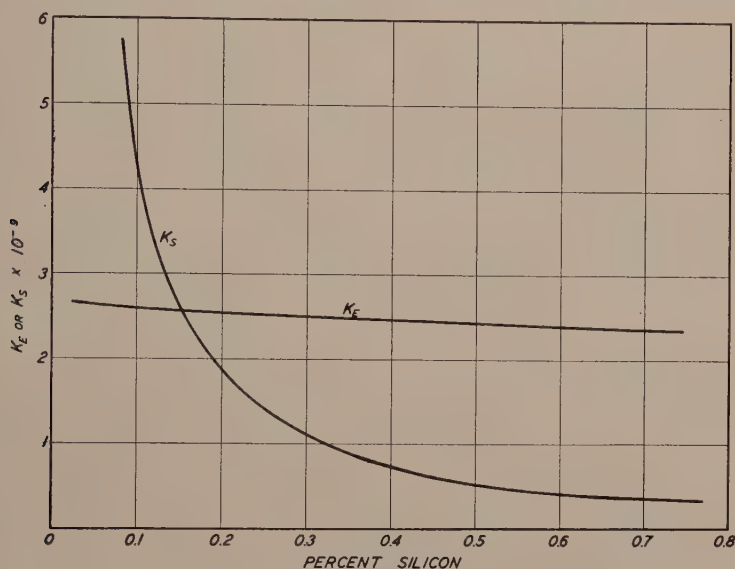


FIG. 7.—INFLUENCE OF SOLUTE CONCENTRATION UPON RATE OF GROWTH OF SUBSCALE K_S AND SURFACE SCALE K_E .

of the subscale is always absent in a narrow zone adjacent to the outside surface of the metal, and that a surface layer of the solute oxide can sometimes be detected on the external surface. It may be deduced from the same observation that internal oxidation does not begin at once upon exposure of an alloy to oxidation at an elevated temperature, but that there is a short preliminary period during which the solute oxidation occurs entirely externally.

It has already been noted that some of the departure of the calculated from the observed rates of oxidation is probably to be associated with the interference of the precipitated oxides with normal diffusion. This conclusion is consistent with the observation that the occurrence of oxides in great profusion or in more or less continuous films in the subscale correspond with unexpectedly small oxidation rates. When external oxidation is also present,

segregate at the external-internal oxide interface. This might well provide a more effective barrier to the passage of oxygen inward or of copper outward than would scattered oxide particles. There does, indeed, seem to be some correspondence between known instances of this kind of segregation and delayed oxidation. Intermittent oxidation, frequently observed among the dilute copper alloys, is probably caused by the periodic spheroidization and reformation of this intermediate layer of the solute oxide.

An interesting side light upon the influence of an alloying element on the relative rates of internal and external oxidation, apart from the blocking effect of the solute oxide, is given by Fig. 7, which has been derived from Eqs. 6 and 7. If the independent rates of growth of the two oxide layers are calculated at a series of silicon contents, it is found that the rate of growth

of the external scale decreases very slowly with increasing silicon, while the rate of growth of the subscale falls off rapidly.

Upon the basis of the mechanism of internal oxidation proposed here, there should be no maximum alloy concentration short of unity above which internal oxidation cannot occur, but a rather definite upper limit is actually found in experiment. Presumably some new mechanism of oxidation appears at the higher alloy concentrations and gradually takes precedence over the simple diffusion mechanism. This aspect of the problem is currently under study, but no conclusions are available at present.

It was at first thought that a measurement of the rate of internal oxidation would provide an indirect means of measuring such constants as C_o , D_o , D_M , or the oxygen-metal ratio in the solute oxide. Attempts to do this led to disappointing results, partly because the errors introduced with the physical data are often cumulative and partly because the rate of oxidation is relatively insensitive to small differences in the values of the individual constants. The diffusion coefficient of oxygen in copper, D_o , can be handled only as a part of the product $C_o D_o$ and therefore can be determined only through a knowledge of C_o . Rather large differences in the value of C_o , if D_o is adjusted accordingly, appear only as a minor factor in the oxidation rate. Thus it is possible to determine $C_o D_o$ but not C_o alone or D_o alone. Likewise D_M , the diffusion coefficient of the solute, has but a small influence upon the rate and cannot be measured in this way. The identification of the oxide (O/M) by this means is feasible in some instances, but frequently the cumulative errors in selecting values of the other constants confuse the result.

SUMMARY

The rates of simple internal oxidation and of combined internal and external oxi-

dation have been measured in a series of 60 dilute binary and ternary alloys of copper over a temperature range from 600° to 1000°C.

It has been shown that, if melting does not occur, internal oxidation occurs between 750° and 1000°C. as a relatively simple diffusion process, which can be described by a mathematical expression. At 600°C. the oxidation process was found to be more complex.

The data have been organized in such a manner as to permit the calculation of the rate of oxidation of any dilute alloy of the systems studied at any temperature within the range of regular behavior.

Methods are presented whereby it is possible to predict with reasonable accuracy the oxidation rates, within the limits of regular behavior, from diffusion and solubility data alone, provided that the compositions of the oxides are known.

ACKNOWLEDGMENTS

The authors wish to express their indebtedness to Mr. Raymond Ward and Mr. Eugene Hughes, who conducted a large part of the experimental work.

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DISCUSSION

(C. E. Swartz presiding)

D. W. SMITH,* New Kensington, Pa.—In presenting the paper, Dr. Rhines mentioned that, according to the better theory of oxidation, copper is diffused through the outside scale and is oxidized on the surface. Does this mean that oxygen does not diffuse through the outside scale surface? If this is true, by what mechanism is the subscale formed?

F. N. RHINES, W. A. JOHNSON AND W. A. ANDERSON (authors' reply).—Dr. Smith's questions are welcome, for they emphasize the speculative nature of the calculations predicting the rates of growth of internal and external oxide layers occurring simultaneously.

There is rather satisfactory evidence, based

largely on measurements of electrical conductivity,¹⁰ that the copper ion diffuses very much more rapidly than the oxygen ion in cuprous oxide. Thus, any theory of the oxidation process should be based on the diffusion of copper, not oxygen. The simplest reasonable process that will supply the necessary oxygen at the interface of the external scale and subscale appears to be the decomposition of a thin layer of cuprous oxide at this interface, with diffusion of the copper outward through the external scale and diffusion of the oxygen inward through the subscale.

It must be admitted that the process may be more complex than the one postulated here and that the rate of the interface reaction, if it occurs as described, may control the over-all rate, but there appears to be no convenient method of clarifying the situation.

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The Constitution of Copper-rich Copper-silicon-manganese Alloys

By CYRIL STANLEY SMITH,* MEMBER, AND WALTER R. HIBBARD, JR.,† STUDENT ASSOCIATE A.I.M.E.

(New York Meeting, February 1942)

IN 1929 one of the authors¹ determined the constitution of copper-silicon-manganese alloys containing over 90 per cent copper. Through a combination of circumstances the presence of the copper-silicon kappa phase was overlooked in both binary and ternary systems. In the binary system the omission has already been rectified.^{2,3} To establish the limits of this phase in the ternary system, the samples that had been heat-treated at the time of the original research have now been re-examined, using more careful technique. Full details of the compositions used and the temperatures and times of heat-treatment are to be found in the earlier paper.² The etching reagent now used to distinguish the kappa phase had the following composition: hydrogen peroxide (30 vol.), 20 c.c.; water, 25 c.c.; 20 per cent potassium hydroxide solution, 5 c.c.; ammonium hydroxide (0.90 sp. gr.), 50 c.c.

Table 1 lists the newly observed structures. In virtually every case the constituents are the same as those previously recorded, except where kappa is now shown to be present as a result of the improved etching technique. A few other changes will be noted (No. 138 at 450°C., No. 147 at 550°C., Nos. 153 and 149 at 750°C.). The change from liquid to beta in equilibrium with kappa in No. 137 at 800°C. is based upon newly heat-treated samples.

Manuscript received at the office of the Institute Nov. 3, 1941. Issued as T.P. 1418 in METALS TECHNOLOGY, January 1942.

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¹ References are at the end of the paper.

The alloy is very near the solidus at 800°C. and probably there was a slight error in the old heat-treatment temperature.

The isothermal phase diagrams shown in Figs. 1 to 6 were reconstructed on the basis of the new studies. The presence of manganese does not greatly change the composition limits of the kappa phase or cause the $\kappa \rightleftharpoons \alpha + \gamma$ change to occur at a markedly different temperature.

There is some uncertainty regarding the range of existence of beta, for alloys were not spaced very closely in composition. The proposed diagrams, however, are in accordance with the available experimental data and with the dictates of the phase rule. Theoretically necessary fields with no experimental points are delineated by dotted lines.

The alpha boundaries at all temperatures are shown together in Fig. 7. This includes also some additional points on the alpha boundary at 300° and 350°C., which were obtained as a result of electrical-conductivity measurements. Two series of seven alloys with increasing manganese content but with silicon constant at 1.90 ± 0.03 per cent or 2.42 ± 0.05 per cent were cast in ingots of 3-in. diameter. These were hot-rolled, homogenized and drawn to wire, finished at 0.08-in. diameter with a 61 per cent reduction of area following annealing at 700°C. Conductivity determinations were made before and after annealing for 30 days at 300°C. or 21 days at 350°C. Figs. 8 and 9 show the change of conductivity produced by this annealing, plotted against manganese

content. The curves are in two branches; one nearly horizontal where the change in conductivity is a result of recovery from

cent Si (Fig. 8) correspond to about 0.35 per cent Mn at 300°C. or 0.55 per cent Mn at 350°C. With 2.42 per cent Si (Fig. 9)

TABLE I.—Structures Recently Observed^a

Specimen No.	Si, Per Cent	Mn, Per Cent	Constituents ^b in Quenched Microspecimens					
			800°C.	750°C.	700°C.	650°C.	550°C.	450°C.
Temperature.....								
Time of Anneal, Hr....			24	24	36	48	72	168
I43	0.96	0.98	I	I	I	I	I	I
I44	1.86	0.88	I	I	I	I	I	I
I45	3.26	0.89	I	I	I	I	I	I + 5°
I46	4.03	0.92	I	I	I	I	I	I + 5°
I47	5.04	0.89	I + 7°	I	I + 7	I + 7	I + 3 + 5	I + 3 + 5
I79	5.54	0.94	I + 7	I + 7	I + 7	7	I + 3 + 5	I + 3 + 5
I48	5.96	1.01	7	7	7		I + 3 + 5	I + 3 + 5
I80	6.54	1.08	2 + 7	7	3 + 7	3 + 7	I + 3 + 5	I + 3 + 5
I49	6.87	1.25	2 + 7	4 + 7	3 + 7	3 + 7	I + 3 + 5	
I50	0.98	1.92	I	I	I	I	I	I
I22	1.76	2.18	I	I	I	I	I	I + 5
I51	3.12	1.77	I	I	I	I	I + 5	I + 5
I31	3.86	1.93	I	I	I	I	I + 5	I + 5
I52	5.01	1.88	I	I + 7	I + 5° + 7	I + 5° + 7	I + 3 + 5	I + 3 + 5
I37	6.04	1.84	2 + 7	7	5 + 7	5 + 7	I + 3 + 5	I + 3 + 5
I53	6.99	1.96	2	4 + 7	4 + 5 + 7	3 + 5 + 7		
I54	1.17	3.12	I	I	I	I	I + 5°	I + 5
I55	1.98	2.93	I	I	I	I	I + 5°	I + 5
I56	3.08	3.12	I	I	I + 5°	I + 5°	I + 5	I + 5
I57	4.07	2.99	I	I + 5°	I + 5°	I + 5	I + 5	I + 5
I58	5.01	3.15	I + 6	I + 5	I + 5° + 7	I + 5	I + 3 + 5	I + 3 + 5
I59	5.95	3.08	I + 2 + 7	5 + 7	I + 5 + 7	3 + 5 + 7		I + 3 + 5
I60	7.13	2.81	2	2 + 5 + 7	4 + 5 + 7	3 + 5 + 7		
I61	1.01	3.82	I	I	I	I	I + 5°	I + 5
I23	1.97	3.94	I	I + 5°	I + 5°	I + 5°	I + 5	I + 5
I62	3.12	3.68	I + 5	I + 5	I + 5	I + 5	I + 5	I + 5
I63	4.00	4.01	I + 5	I + 5	I + 5	I + 5	I + 5	I + 5
I32	4.21	4.32	I + 5	I + 5	I + 5	I + 5	I + 5	I + 5
I64	5.02	3.92	I + 6	I + 5	I + 5	I + 5	I + 5	I + 3 + 5
I38	6.19	3.86	I + 6	5 + 7	5 + 7	5 + 7	I + 3 + 5	I + 3 + 5
I65	6.77	4.34	2 + 6	2 + 5 + 7	4 + 5 + 7	3 + 5 + 7		
I66	1.05	4.59	I	I	I + 5°	I + 5°	I + 5	I + 5
I24	2.01	5.23	I + 5°	I + 5	I + 5	I + 5	I + 5	I + 5
I67	2.98	4.85	I + 5	I + 5	I + 5	I + 5	I + 5	I + 5
I68	3.97	5.03	I + 5	I + 5	I + 5	I + 5	I + 5	I + 5
I69	4.93	5.12	I + 5 + 6	I + 5	I + 5	I + 5	I + 5	I + 5
I70	1.04	5.58	I + 5°	I + 5	I + 5	I + 5	I + 5	I + 5
I71	2.01	5.73	I + 5	I + 5	I + 5	I + 5	I + 5	I + 5
I72	3.03	6.10	I + 5	I + 5	I + 5	I + 5	I + 5	I + 5
I33	3.75	5.85	I + 5	I + 5	I + 5	I + 5	I + 5	I + 5
I73	1.05	6.65	I + 5°	I + 5	I + 5°	I + 5	I + 5	I + 5
I74	1.93	6.35	I + 5	I + 5	I + 5	I + 5	I + 5	I + 5
I75	2.96	6.72	I + 5	I + 5	I + 5	I + 5	I + 5	I + 5
I76	1.03	7.64	I + 5	I + 5	I + 5	I + 5	I + 5	I + 5
I77	2.01	7.68	I + 5	I + 5	I + 5	I + 5	I + 5	I + 5
I78	1.06	8.56	I + 5	I + 5	I + 5	I + 5	I + 5	I + 5

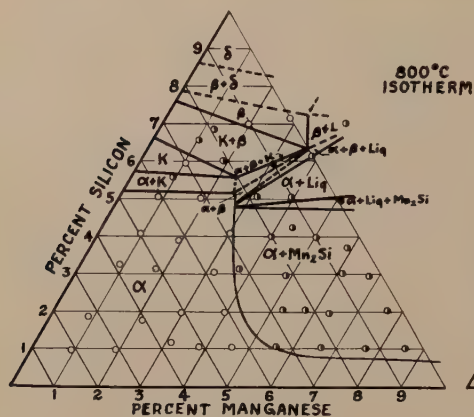
^a See reference 1 for experimental details. Alloys were homogenized and where possible cold-worked before annealing. Compositions are given in percentages by weight.

^b I, alpha; 2, beta; 3, gamma; 4, delta; 5, manganese silicide; 6, liquid; 7, kappa.

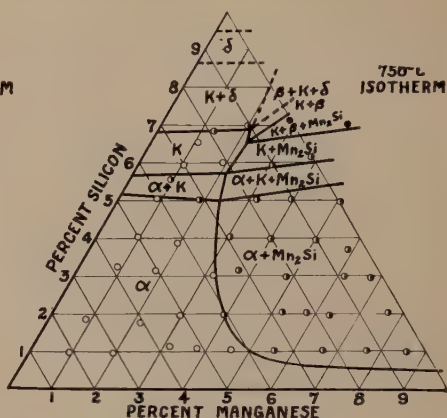
^c Trace.

cold-work alone, and the other sloped as a result of the increasing precipitation of Mn_2Si from solution. The points of intersection in the series with 1.90 per

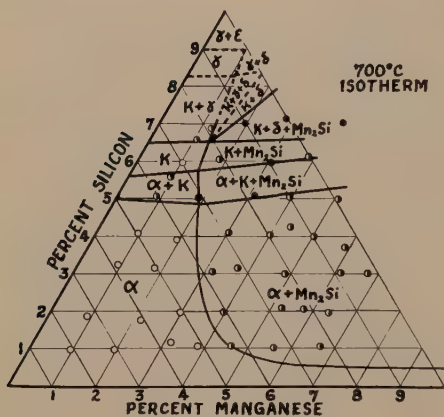
the indicated solubilities are 0.3 per cent Mn at 300°C. and 0.45 per cent Mn at 350°C. Precipitation was relatively rapid in these cold-worked alloys; 50 per cent



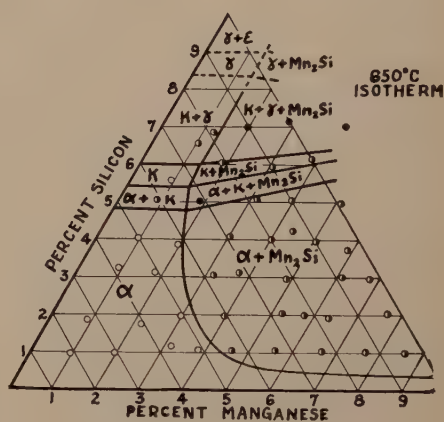
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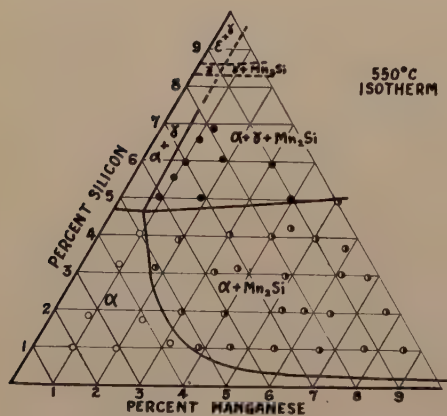
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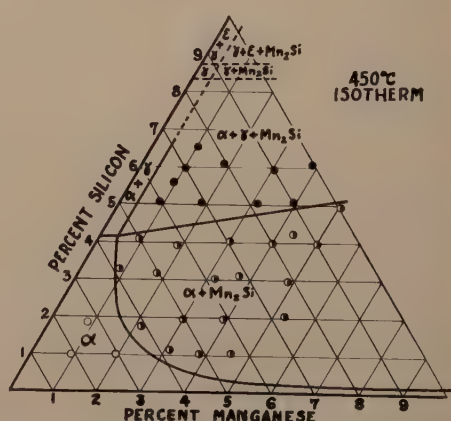
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5



6

FIGS. 1-6.—ISOTHERMAL SECTIONS OF THE TERNARY CONSTITUTION DIAGRAM. Plotted according to percentages by weight.

of the entire change of conductivity occurred in 2 hr. at 350°C. Wire quenched from 700°C. without cold-working showed

looked. The results are presented in the form of isothermal phase diagrams at temperatures between 450° and 800°C.

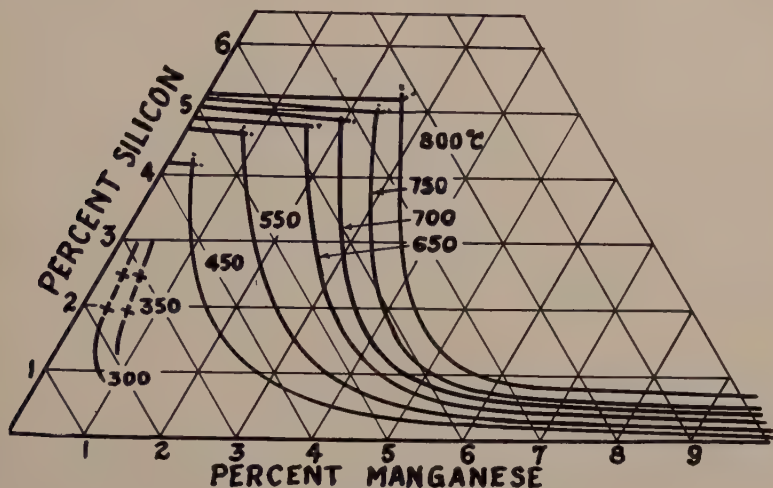
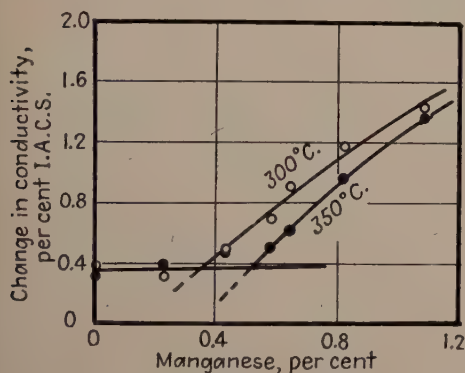


FIG. 7.—ALPHA-PHASE BOUNDARIES IN THE COPPER-SILICON-MANGANESE SYSTEM AT VARIOUS TEMPERATURES.



FIGS. 8 AND 9.—CHANGE OF CONDUCTIVITY ON ANNEALING COPPER-SILICON-MANGANESE ALLOYS.

Fig. 8.—Silicon constant at 1.90 ± 0.03 per cent; manganese 0 to 1.1 per cent as plotted.

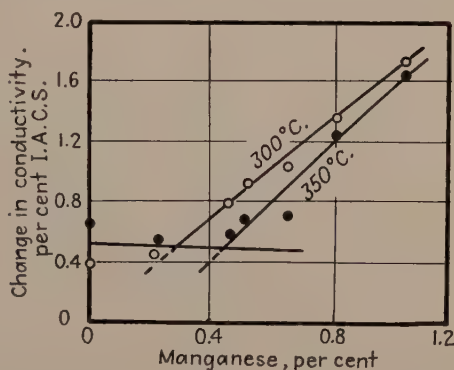


Fig. 9.—Silicon constant at 2.42 ± 0.05 per cent; manganese 0 to 1.1 per cent as plotted.

virtually no change in conductivity after annealing 30 days at 300°C.

SUMMARY

A re-examination of the microsamples heat-treated in an earlier research on the constitution of copper-silicon-manganese alloys with over 90 per cent copper has shown the extent of the domain of the kappa phase that was previously over-

Conductivity measurements have extended a portion of the alpha boundary to a temperature of 300°C.

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2. C. S. Smith: Constitution and Microstructure of Copper-rich Silicon-copper Alloys. *Trans. A.I.M.E.* (1940) **137**, 313-328.
3. A. G. H. Andersen: The Alpha Solubility Limit and the First Intermediary Phase in the Copper-silicon System. *Trans. A.I.M.E.* (1940) **137**, 334-350.

Effect of Columbium on Some Annealing Characteristics of Copper and 80-20 Cupronickel

By ALAN U. SEYBOLT,* MEMBER A.I.M.E.

(Philadelphia Meeting, October 1941)

IN examination of some cold-rolled copper and cupronickel that contained a little columbium, it was discovered that these alloys were unusually resistant to annealing. This effect was sufficiently pronounced to warrant some investigation

This hardener alloy contained 10 per cent columbium, with tantalum, aluminum and iron as major impurities.

The melting was carried out in a clay-graphite crucible in a high-frequency induction furnace, under a charcoal or

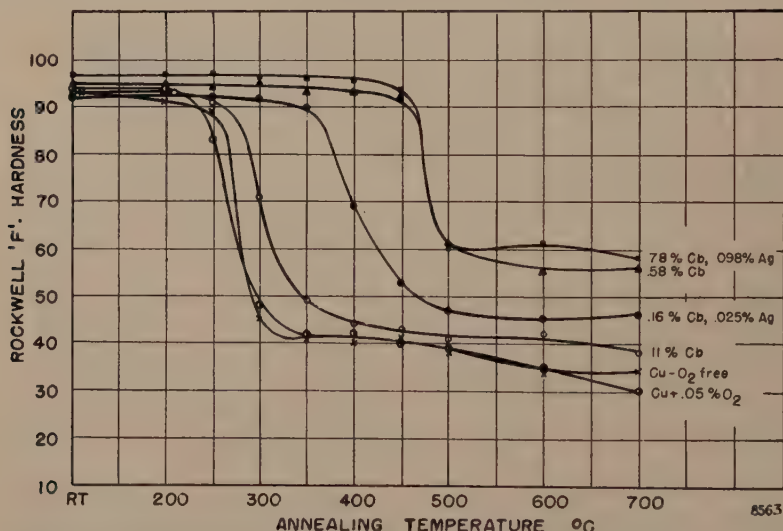


FIG. 1.—EFFECT OF COLUMBIUM ON HARDNESS OF COPPER AFTER ANNEALING FOR $\frac{1}{2}$ -HOUR PERIODS AT INDICATED TEMPERATURES.

of the annealing characteristics of such compositions.

EXPERIMENTAL PROCEDURE

The alloys were made from cathode copper, electrolytic nickel, and a special copper-columbium hardener alloy furnished by the Electro Metallurgical Corporation.

Manuscript received at the office of the Institute Feb. 10, 1941. Issued as T.P. 1342 in METALS TECHNOLOGY, August 1941.

* Metallurgist, Battelle Memorial Institute, Columbus, Ohio.

electrode carbon cover. No deoxidizing additions were made. The 7-lb. copper heats were poured into a steel mold, hot-rolled to $\frac{1}{4}$ -in. thickness, and annealed for $\frac{1}{2}$ hr. at 760°C.; the cupronickels were annealed 1 hr. at 815°C. The material was then cold-rolled to a 50 per cent reduction in thickness and annealing tests were carried out on this $\frac{1}{8}$ -in. hard-rolled strip.

A little silver was added to copper-columbium alloys 402 and 403 to find out

whether silver would raise the annealing temperature over the level obtained without silver. No definite microscopic evidence of oxygen was found in any of the copper ingots except in the control, which contained no columbium. Later another control heat of unalloyed copper was cast and found to be microscopically free of cuprous oxide. For sake of brevity, this copper was termed oxygen-free, although it may have contained slightly more oxygen than the limit of solid solubility.

EXPERIMENTAL RESULTS

Hardness of the Copper-columbium Alloys after Annealing.—It appears from the results

bium phase are readily observed, and some of the columbium phase in the alloy of higher columbium content is segregated in the rolling direction.

The two coppers of highest columbium content soften somewhat with increasing time at $450^{\circ}\text{C}.$, as shown in Fig. 4, but it is clear that after 24 hr. they are still incompletely recrystallized. The somewhat high hardness of the copper containing 0.11 per cent Cb after a treatment for 2 hr. at $300^{\circ}\text{C}.$ is possibly due to some age-hardening.

Electrical Conductivity.—The rather low electrical conductivity values, particularly in alloys 401 and 403, are probably due mostly to the iron and aluminum content,

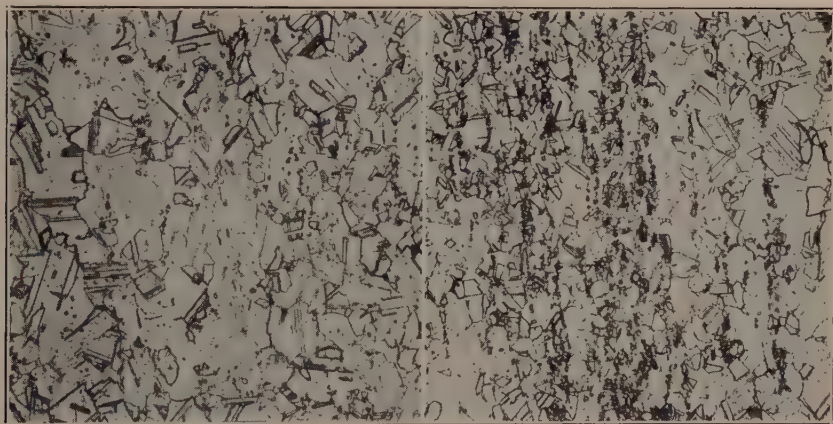


FIG. 2.

FIG. 3.

FIG. 2.—COPPER + 0.16 PER CENT COLUMBIUM ANNEALED FOR $\frac{1}{2}$ HOUR AT $700^{\circ}\text{C}.$ $\times 200.$

FIG. 3.—COPPER + 0.58 PER CENT COLUMBIUM ANNEALED FOR $\frac{1}{2}$ HOUR AT $700^{\circ}\text{C}.$ $\times 200.$

shown in Fig. 1 that silver plays a very minor role in copper with relatively large amounts of columbium. Also, the copper with 0.16 per cent Cb and 0.025 per cent Ag does not become completely soft until a temperature of about $500^{\circ}\text{C}.$ is reached, while copper containing 0.025 per cent Ag (with no columbium) becomes fully soft at about $325^{\circ}\text{C}.$ ¹

The microstructures of two of the copper-columbium alloys are shown in Figs. 2 and 3. The larger particles of the colum-

rather than to the columbium content. Addicks² has shown that with 0.16 per cent Al in copper, the amount occurring in alloy 403 (Table 1), the electrical conductivity is reduced to about 61 per cent that of pure copper. Hanson and Ford³ found that 0.14 per cent Fe lowers the conductivity of copper to about 70 per cent that of the pure metal.

Tensile Tests.—The tensile-test results given in Table 3 are in qualitative agreement with the curves for hardness versus temperature.

¹ References are at the end of the paper.

Hardness of the Cupronickel Alloys after Annealing.—Figs. 6 and 7 show that columbium has a similar effect upon the annealing characteristics of cupronickel, although the increase in the softening temperature is not as much as in the coppers.

istics of copper shows that 0.14 per cent Fe would have an almost negligible effect upon the softening temperature of pure copper. Similarly, the work of O. Dahl⁴ indicates that 0.10 per cent Al causes a softening temperature of about 250°C., while Hud-

TABLE I.—Composition of the Alloys

Alloy No.	Cb Added, Per Cent	Cb Recovery, Per Cent	Chemical Analysis, Per Cent					
			Cb	Ta	Fe	Al	Cu	Ag
Coppers:								
312 ^a					0.012	0.005		
427.....					0.018	0.005		
398.....	0.33	33.0	0.11		0.056	0.042		
401.....	1.3	44.5	0.58		0.098	0.18		
402.....	0.33	48.5	0.16		0.042	0.058		0.025
403.....	1.3	60.0	0.78	0.16	0.14	0.16		0.098
80-20 Cupronickels:								
315.....					0.049	0.005		
316.....	0.1	74.0	0.074		0.026	0.003	80.17	
317.....	0.3	96.8	0.29		0.041	0.003	79.72	

^a Copper No. 312 contained 0.05 per cent oxygen as estimated by microscopic examination.

DISCUSSION OF RESULTS

While it is realized that the presence of appreciable amounts of iron, aluminum and tantalum may have exerted some effect upon the annealing characteristics of the

son, Herbert, Ball and Bucknall⁵ found that 0.50 per cent Al raises the softening temperature of copper to 300°C.

Judging from the sources quoted, the combined effect of iron and aluminum

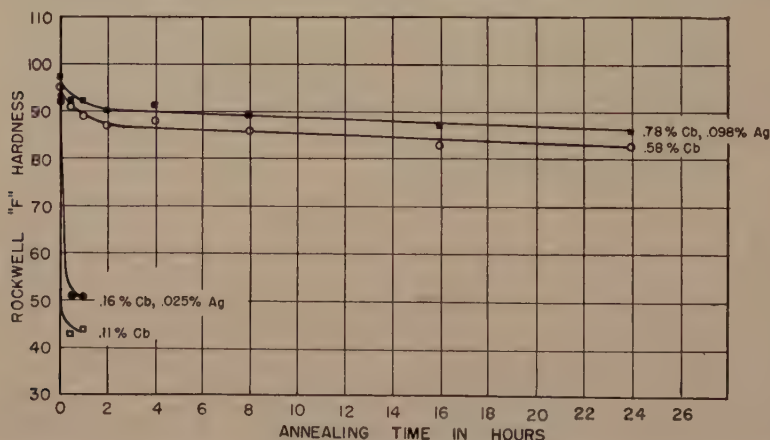


FIG. 4.—EFFECT OF COLUMBIUM ON THE HARDNESS OF COPPER AFTER ANNEALING FOR VARIOUS PERIODS OF TIME AT 450°C.

alloys investigated, the amounts of these elements are all very low compared to the columbium content.

The work of Hanson and Ford³ on the effect of iron on the annealing character-

istics of copper would not appear to have caused more than a 50°C. rise in the softening temperature; thus the relatively large increase obtained with columbium (contaminated

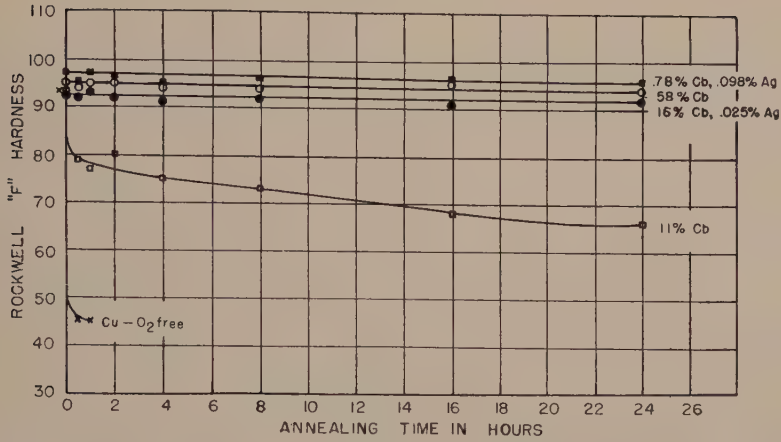


FIG. 5.—EFFECT OF COLUMBIUM ON HARDNESS OF COPPER AFTER ANNEALING FOR VARIOUS PERIODS OF TIME AT 300°C.

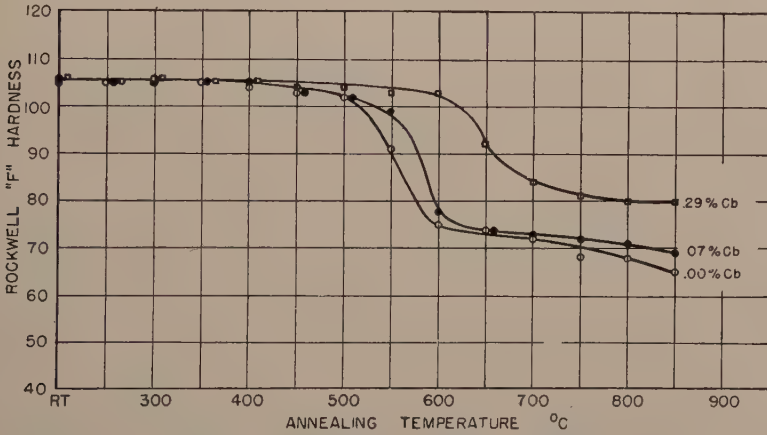


FIG. 6.—EFFECT OF COLUMBIUM ON HARDNESS OF 80-20 CUPRONICKEL AFTER ANNEALING FOR $\frac{1}{2}$ -HOUR PERIODS.

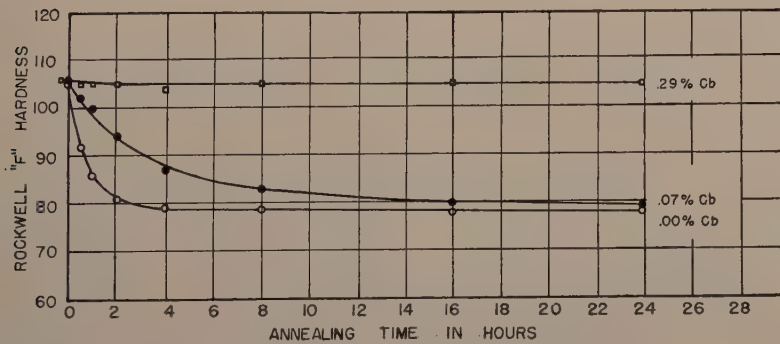


FIG. 7.—EFFECT OF COLUMBIUM ON HARDNESS OF 80-20 CUPRONICKEL AFTER ANNEALING FOR VARIOUS PERIODS OF TIME AT 550°C.

with iron and aluminum) may be ascribed primarily to the columbium.

Since Figs. 2 and 3 show many large particles of columbium, it would be expected that a smaller amount of columbium would

TABLE 2.—*Electrical Resistivity of Copper-columbium Alloys*
MICROHM-CENTIMETERS

Alloy No.	Cb, Per Cent	Resistivity	Conductivity, Per Cent, I.A. C.S. Standard	Condition
427	0	1.71	101	Cold-rolled
427	0	1.71	101	Annealed $\frac{1}{2}$ hr. 200°C.
312	0	1.74	99	Cold-rolled
312	0	1.74	99	Annealed $\frac{1}{2}$ hr. 200°C.
398	0.11	2.14	81	Cold-rolled
398	0.11	2.14	81	Annealed $\frac{1}{2}$ hr. 200°C.
402	0.16	2.26	76	Cold-rolled
402	0.16	2.12	81	Annealed $\frac{1}{2}$ hr. 300°C.
401	0.58	3.06	56	Cold-rolled
401	0.58	2.98	59	Annealed $\frac{1}{2}$ hr. 450°C.
403	0.78	3.23	53	Cold-rolled
403	0.78	3.14	55	Annealed $\frac{1}{2}$ hr. 450°C.

TABLE 3.—*Results of Tensile Tests*

Alloy No.	Cb, Per Cent	Tensile Strength, 1000 Lb. per Sq. In.		Yield Strength, ^a 1000 Lb. per Sq. In.	Elongation in 2 In. Per Cent	
		Cold-rolled	Annealed $\frac{1}{2}$ Hr. 450°C.		Cold-rolled	Annealed $\frac{1}{2}$ Hr. 450°C.
312	0	51.3	31.8	13.3	6.0	52.5
398	0.11	51.2	33.0	9.6	6.0	50.3
403	0.78	55.7	48.3	45.8	5.0	12.3

^a 0.2 per cent offset.

be just as effective in raising the softening temperature if a better dispersion were obtained.

Because of the high softening temperature of copper-columbium, certain operations involving heating may be possible with this material that are not practicable with lake or other annealing-resistant coppers.

CONCLUSIONS

1. The addition of 0.58 per cent Cb with associated impurities raised the softening temperature of cold-rolled copper to about 450°C., compared to about 250°C. for pure copper.

2. About 0.1 per cent Cb in copper is required to produce a noticeable effect in raising the softening temperature.

3. The addition of 0.29 per cent Cb to 80-20 cupronickel raises the softening temperature of the cold-rolled alloy to about 600°C. compared with about 500°C. for the cupronickel without columbium.

ACKNOWLEDGMENTS

The author is grateful to the Union Carbide and Carbon Research Laboratories, Inc., for which this investigation was undertaken, for permission to publish this paper. Thanks are extended to Dr. A. B. Kinzel, of that organization, and to Dr. Bruce Gonser, of Battelle Memorial Institute, for helpful counsel during the work. The efficient and valuable help of Mr. Robert Ramsey, who performed much of the mechanical testing and metallographic preparation, is gratefully acknowledged.

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2. L. Addicks: *Trans. A.I.M.E.* (1906) 36, 18.
3. D. Hanson and G. W. Ford: *Jnl. Inst. Metals* (1924) 32, 335.
4. O. Dahl: *Wissenschaft. Veröff. Siemens-Konzern* (1929) 8, 2.
5. Hudson, Herbert, Ball and Bucknall: *Jnl. Inst. Metals* (1929) 42, 221.

DISCUSSION

(C. E. Swartz presiding)

C. S. SMITH,* Waterbury, Conn.—Tantalum added to commercially pure copper has an effect exactly the opposite of that reported by the author for columbium. Instead of raising the recrystallization temperature, it lowers it. Tantalum seems to be soluble in molten copper up to about 0.025 per cent and additions beyond this sink undissolved to the bottom of the melt. This amount of tantalum deoxidizes

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copper unless it is poured under strongly oxidizing conditions. The conductivity in a series of samples with excess tantalum ran 100.2 to 100.6 per cent I.A.C.S. and the wires

particles. Silver is an example of the first sort and columbium seems to be an example of the second. Tantalum would be expected to behave like columbium. However, there seems to be

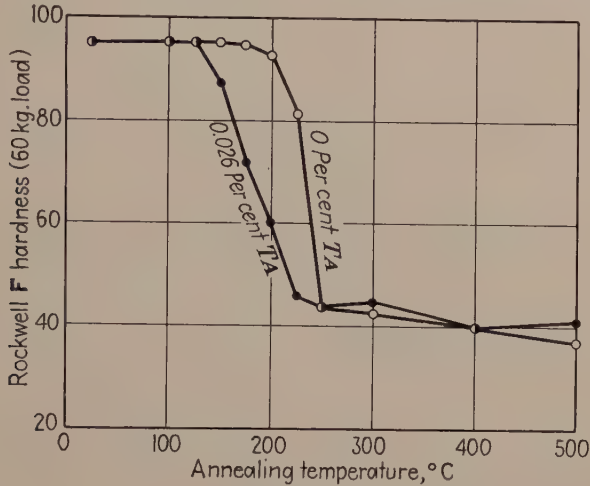


FIG. 8.—CHANGE OF HARDNESS OF TANTALUM-COPPER ALLOY.

withstood 13 to 20 bends after the annealing in hydrogen for 30 min. at 850°C. Fig. 8 shows the change of hardness on reheating of strips cold-rolled 77 per cent reduction to 0.040 in. after annealing at 800°C. The strip containing 0.026 per cent tantalum by analysis (0.2 per cent tantalum added) actually starts to soften at a temperature 75°C. below that of the tantalum-free N.E.C. copper strip. Supposedly the tantalum removed some soluble impurities and it is not itself sufficiently soluble to affect recrystallization, or, if soluble, does not change in solubility appreciably with temperature.

W. B. PRICE,* Waterbury, Conn.—We have found that magnesium seems to have the same effect as columbium on 18 per cent nickel silver and 80-20 and 70-30 cupronickel. As low as two thousandths of one per cent magnesium will show unusual resistance to annealing.

A. U. SEYBOLT (author's reply).—Dr. Smith's comment that tantalum in copper may not be "sufficiently soluble to affect recrystallization" should perhaps be amplified a little. Apparently an added element can affect the recrystallization temperature of copper by two different methods: (1) by being in solid solution, and (2) by being dispersed in a fine mist of insoluble

evidence that in order to show the second effect (recrystallization inhibition by dispersion) a certain minimum amount of the dispersed element must be present. It is not surprising that 0.026 per cent tantalum failed to cause any increase in the recrystallization temperature, (or that the recrystallization temperature was actually lowered if a refining effect occurred).

In order to be effective, the insoluble phase must be quite finely divided and, of course, well distributed. The effect of columbium in the coppers was more pronounced than in the cupronickels, perhaps because of the solubility relations. Since columbium appears to be more soluble in cupronickel than in copper, it might be anticipated that the columbium particle size would be smaller in the latter. In any case, the spread in recrystallization temperature in the cupronickels with and without columbium was only about 100°C. compared with about 200°C. for the copper.

Mr. Price's statement that only two thousandths of one per cent magnesium in cupronickel causes unusual resistance to annealing suggests that a fine dispersion of magnesia may be responsible for the effect. It is difficult to see how so little of any element in *solution* in alloys of ordinary purity could have a marked influence on the softening temperature.

* Chief Chemist and Metallurgist, Scovill Manufacturing Co.

The Ferromagnetic Nature of the Beta Phase in the Copper-manganese-tin System

BY LOUIS A. CARAPELLA* AND RALPH HULTGREN,† MEMBER A.I.M.E.

(Philadelphia Meeting, October 1941)

WHEN F. Heusler¹ found in 1898 that certain alloys containing only copper, manganese, and tin were ferromagnetic, the discovery excited a great deal of interest and led to numerous investigations. It was early found that tin could be replaced by aluminum, arsenic, antimony, bismuth, or boron without destroying the ferromagnetic nature of the alloys.² Copper may also be replaced by silver.³ All these alloys have come to be known as "Heusler alloys." The aluminum alloys apparently were the most magnetic and have been most extensively investigated. However, no agreement has yet been reached as to the source of the ferromagnetism arising from these nonferromagnetic elements. Absence of reliable quantitative data makes speculation hazardous.

The value of much of the earlier work was vitiated by lack of necessary precautions against contamination, and by lack of close control of heat-treatment. It was only recently established that in aluminum Heusler alloys⁴ the ferromagnetism arose from a single phase, an ordered body-centered-cubic structure.

With modern methods of preparation, heat-treatment, and X-ray examination, it is possible to prepare these alloys without contamination, to heat-treat them intelligently, and to determine what phase or phases are present in the finished sample. In the present investigation, a series of pure alloys in the comparatively neglected copper-manganese-tin system have been prepared, which consist of a single, body-centered-cubic structure (the beta phase) and whose compositions vary within wide limits. The magnetic saturation values of these single-phase alloys have been quantitatively determined, so that considerable data on the effect of composition on the ferromagnetism have been made available. In the course of the investigation some information on the extent of the stability of the beta phase and the nature of phases in adjacent regions of the ternary diagram has been accumulated. Anomalies in earlier data have been explained, and alloys have been prepared that are much more strongly magnetic than any previous Heusler alloys.

PREVIOUS WORK

In the original work of F. Heusler¹ and coworkers,² a maximum magnetic saturation value of $I = 107$ was found at the composition $\text{Cu}_6\text{Mn}_3\text{Sn}$, while a value for Cu_2MnAl of $I = 443$ was early measured. Ross and Gray⁵ found a second maximum at the composition Cu_2MnSn , which was much more magnetic than Heusler's original alloy. F. Heusler⁶ then reinvestigated the system, confirmed their results,

Most of the material presented in this paper was abstracted from a thesis submitted by Louis A. Carapella in partial fulfillment of the requirements for the degree of Doctor of Science, Harvard University, 1941. Manuscript received at the office of the Institute June 10, 1941. Issued as T.P. 1495 in METALS TECHNOLOGY, October 1941.

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† Assistant Professor of Metallurgy, Graduate School of Engineering, Harvard University; now Assistant Professor of Physical Metallurgy, University of California, Berkeley, California.

¹ References are at the end of the paper.

and obtained a value about as high as that of the aluminum alloy. Take and Semm⁷ made a systematic survey of magnetism in the ternary system, publishing the mag-

netic saturation values for the copper-manganese-tin system. The ordered structure was designated β' and was found to extend over a considerable range of composition within the beta phase. Pers-

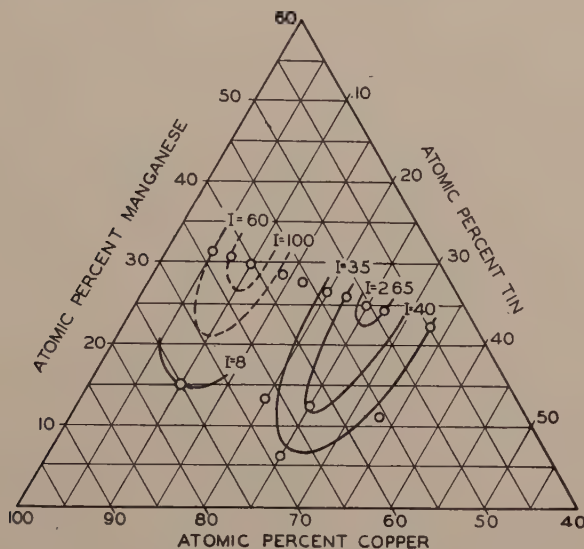


FIG. 1.—ISOMAGNETIC SATURATION CONTOURS FOR THE COPPER-MANGANESE-TIN SYSTEM. According to Take and Semm.⁷

son found that the Cu_2MnSn alloy was also ordered, suggesting that this system was analogous to the aluminum system, but did not pursue the subject further.

son found that the Cu_2MnSn alloy was also ordered, suggesting that this system was analogous to the aluminum system, but did not pursue the subject further. Aside from this single observation, the copper-manganese-tin Heusler alloys have received little attention since the work of Take and Semm in 1914. Verö¹⁰ studied the copper-rich portion of the ternary system by thermal and microscopic methods in 1933, but his results indicating a small range of homogeneity for beta manganese bronzes are contradicted by the present investigation. Few quantitative data are available concerning the effect of composition on magnetizability. The only investigation in which the crystal structure was controlled was the work of O. Heusler.⁹ He measured magnetic saturation values along two section lines of the copper-manganese-aluminum system.

Although early investigators realized that heat-treatment had profound effects on magnetizability, it was not until 1932 that Persson⁴ was able to show that all the magnetic alloys in the copper-manganese-aluminum system contained a body-centered-cubic (beta) phase. At the composition with the maximum saturation value, Cu_2MnAl , the aluminum atoms formed a face-centered superlattice. Since this superlattice was present in all magnetic alloys, Persson concluded that it alone was ferromagnetic. Later, Bradley and Rodgers⁸ and O. Heusler⁹ found independently, by a special X-ray technique, that copper and manganese atoms also

occupied ordered positions. The ordered structure was designated β' and was found to extend over a considerable range of composition within the beta phase. Pers-

son found that the Cu_2MnSn alloy was also ordered, suggesting that this system was analogous to the aluminum system, but did not pursue the subject further. Aside from this single observation, the copper-manganese-tin Heusler alloys have received little attention since the work of Take and Semm in 1914. Verö¹⁰ studied the copper-rich portion of the ternary system by thermal and microscopic methods in 1933, but his results indicating a small range of homogeneity for beta manganese bronzes are contradicted by the present investigation. Few quantitative data are available concerning the effect of composition on magnetizability. The only investigation in which the crystal structure was controlled was the work of O. Heusler.⁹ He measured magnetic saturation values along two section lines of the copper-manganese-aluminum system.

MATERIALS

High-quality materials were used in preparing alloys for this investigation. Specially prepared high-purity electrolytic

Works was also spectroscopically analyzed and estimated to be 99.999 per cent pure. The lattice constant was $a_0 = 3.6073 \text{ \AA}$, compared with the value of Hume-Rothery,

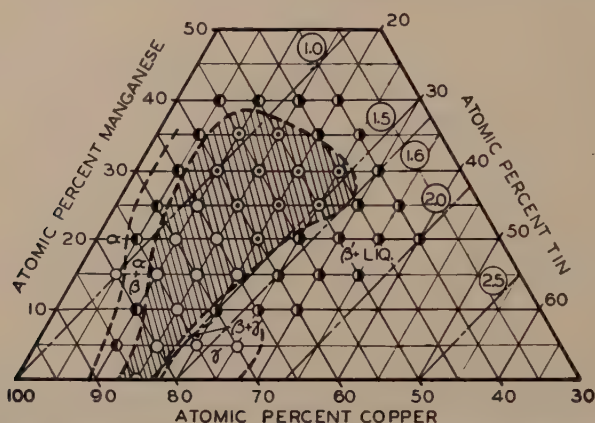


FIG. 2.—BETA-PHASE RANGE (SHADED AREA) OF COPPER-MANGANESE-TIN SYSTEM. (This is not an isothermal section.)

- ⊙ = evidence of long-range ordering (beta-prime phase).
- = absence of long-range ordering.
- ⊗ = two or more phases.

Electron-atom ratios are indicated by broken lines.

manganese was obtained from the Electro-Manganese Corporation.* A spectroscopic analysis† shows the following impurities: Fe, 0.002 per cent; Si, 0.001; Mg, 0.005; Ca, 0.001; Ti, trace; V, trace; Al, trace; Co, absent; Cu, absent; Ni, absent; estimated purity, 99.991 per cent.

The lattice constant‡ in the alpha modification was determined by precision methods^{11,12,13} and found to be

$$a_0 = 8.8959 \text{ \AA}.$$

This compares with the value of Johannsen and Nitka,¹⁴ $a_0 = 8.8964 \text{ \AA}$, for alpha manganese having a purity of 99.95 per cent.

High-purity electrolytic copper generously supplied by the Raritan Copper

Levin and Reynolds,¹⁵ $a_0 = 3.6075 \text{ \AA}$, for high-purity copper.

Tin of high purity was kindly furnished by the International Tin Research and Development Council. The only notable impurity was lead, about 0.003 per cent, while the total purity was estimated as 99.992 per cent. Lattice constants were found to be $a_0 = 5.8197 \text{ \AA}$, $c_0 = 3.1750 \text{ \AA}$, and $c_0/a_0 = 0.5456$, in close agreement with the values of Jette and Foote¹² for tin of a purity of 99.995 per cent. Their values were 5.81950 \AA , 3.17500 \AA , and 0.54557 , respectively.

PREPARATION OF ALLOYS

Alloys were prepared by melting together weighed quantities of the three constituents and homogenizing the ingots by prolonged annealing. Filings were then taken, or part of the ingot was pulverized, if it was very brittle. In some cases, slivers were sawed out. The resulting samples were given

* We are particularly indebted to Mr. K. M. Leute, president of Electro-Manganese Corporation, Knoxville, Tennessee, for supplying several shipments of electrolytic manganese of exceptionally high grade.

† All spectroscopic analyses of materials used were made by Mr. J. Sterner, of the Baird Associates, Cambridge, Mass.

‡ Lattice constants are corrected to 25°C.

the desired heat-treatment and rapidly quenched.

Molten manganese attacks silica and carbon, so the crucible material must be chosen with care. Jay¹⁶ had suggested alumina, and pure alumina crucibles prepared without binder by the Lava Crucible Company of Pittsburgh were used with success.

Manganese is too volatile to melt in a vacuum, it produces a magnetic hydride when melted under hydrogen,¹⁷ and Walters¹⁸ reports that it combines with nitrogen and suggests argon as suitable for a protective atmosphere. All melts were made in an atmosphere of argon gas obtained from the Air Reduction Sales Co. They report the analysis to be 99.6 per cent argon and 0.4 per cent nitrogen.

Alloys were prepared by thoroughly mixing filings of copper, manganese, and tin and melting them at 1100°C. The crucible was vigorously shaken to ensure mixing and the alloy was retained in the molten state for about 15 min., then quenched to prevent excessive segregation.

The resulting ingots, weighing about three grams, were sealed in vacuo in Pyrex or Vitreosil tubes and given a homogenizing anneal just below the solidus temperature, for two to three weeks. Homogeneity was checked by microscopic examination, and, finally, by X-ray diffraction patterns of filings taken from various portions of the same ingot, mixed, and annealed. Sharp lines were considered to show the alloy to be homogeneous.

Ingots were filed or pulverized, sealed in evacuated Pyrex glass* tubes and annealed at accurately controlled temperatures for 18 to 24 hr. The glass capsules were then expelled from the furnace by a ramrod and broken on an anvil under water, providing an almost instantaneous quench. The technique has been previously described in

publications from this laboratory.¹⁹ The resulting sample was washed with alcohol, dried, and separated from the glass magnetically, or if the sample were nonmagnetic, much of the glass could be removed by screening. The powders were then ready for X-ray diffraction and magnetic studies.

Many of the ingots adhered to the rough walls of melting crucibles and were removed by breaking the crucibles. Each ingot was cleaned by grinding off a slight surface layer. There was no noticeable contamination. The desired compositions were carefully weighed out, and, barring systematic loss of one of the constituents, should form an alloy of the weighed composition. Manganese, because of its volatility and reactivity, is the only one likely to be lost in appreciable quantities. A number of chemical analyses of ingots were made, some by Dr. H. H. Anderson of Harvard University, and some by Dr. G. G. Marvin of the Massachusetts Institute of Technology. Because of difficulties in the analysis, only a few of the ingots were analyzed. The results indicated that manganese was not being lost and that the compositions of the ingots were close to those weighed out.

X-RAY RESULTS

The phases present were identified by powder X-ray diffraction methods. Single-phase samples consisting entirely of body-centered-cubic (beta) structure were prepared over as wide a range of compositions as possible. It was found that the beta phase is stable only at elevated temperatures but can be retained by quenching. By choosing suitable annealing temperatures below the solidus and above the temperature of decomposition, it is possible to prepare beta phases over the wide range of compositions shown in Fig. 2. The annealing temperature used varied from 640° to 715°C. Some information also was obtained on the nature of phases in neighboring regions. The results are indicated in the

* Pyrex No. 172 was found to withstand temperatures as high as 750°C. for over a week without failure.

figure. No attempt was made to identify the products of beta-phase decomposition at lower temperatures.

The observation of Persson that Cu_2 -

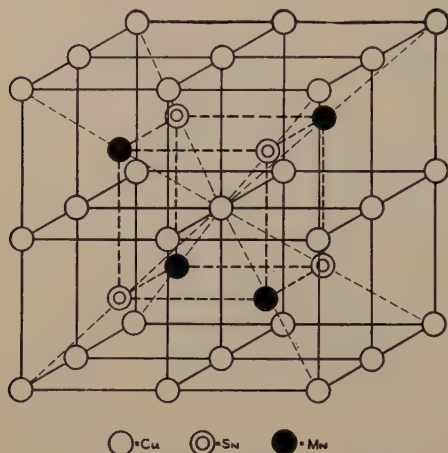


FIG. 3.—ORDERED STRUCTURE OF Cu_2MnSn .

MnSn was body-centered-cubic, and that the tin atoms were ordered like the aluminum atoms in Cu_2MnAl was confirmed, and it was found that the ordering persisted over a considerable range of composition. At compositions far from ideal, it is possible to have considerable order even though superlattice lines are not detected, so their absence cannot be regarded as conclusive proof of lack of order. No evidence of a "Curie point of ordering" was obtained; the alloys seem to remain ordered to the melting point. An X-ray photogram of Cu_2MnSn at 630°C . taken in a high-temperature diffraction camera showed the presence of superlattice lines.

By taking advantage of anomalous dispersion near the absorption edge of elements, it is possible to detect ordering among the copper and manganese atoms. This has been done by Bradley and Rodgers⁸ and by O. Heusler⁹ in the copper-manganese-aluminum superlattice. Ordering will cause certain of the superlattice lines to be relatively weaker with iron radiation than with copper. Such a weakening of

these lines is definitely observed in the tin alloy, so the ordering is verified and the structure must be as shown in Fig. 3. A precise determination of lattice constant for the structure was made and it was found that $a_0 = 6.1608 \text{ \AA}$.*

MAGNETIC WORK

Magnetic saturation values of all samples consisting of the beta phase alone were determined by a magnetometer constructed after a design of Fereday.²⁰ It contains 23,400 turns of wire wound about spools surrounding pole pieces of Armco iron. An inhomogeneous field was produced by making one pole piece smaller than the other. A small ferromagnetic sample placed between the pole pieces is attracted toward the smaller by a force (in dynes) equal to:

$$f = m\sigma \frac{dH}{dx}$$

where:

m = mass of specimen, grams,

σ = magnetization (ergs per gauss per gram),

dH/dx = rate of change of field intensity, oersteds per centimeter.

By a suitable choice of relative sizes of the pole pieces, and by making the larger one concave, the value of dH/dx can be made uniform over a considerable zone. Then the magnetization of a specimen of unit mass is proportional to the force. This force may be conveniently measured with a torsion balance.²¹ Nickel shot, which was found by Prof. A. Kaufman, of the Massachusetts Institute of Technology, to have a saturation moment practically equal to that given in the literature,²² was used for calibration. The calibration was repeated before and after each series of measurements.†

Although a small field is sufficient to saturate a rounded piece of iron, irregularly shaped objects and powders are more diffi-

* Corrected to 25°C .

† For a detailed description of the design and performance of the magnetometer and torsion balance, see thesis.

cult because of the demagnetizing effect. For this reason, the apparatus was made of a large capacity (23,400 turns carrying 2.5 amp.). The field obtained amounted to

obtained are shown in Fig. 4 and given in Table I.

It was noted that in several cases slivers were more magnetic than powders of the

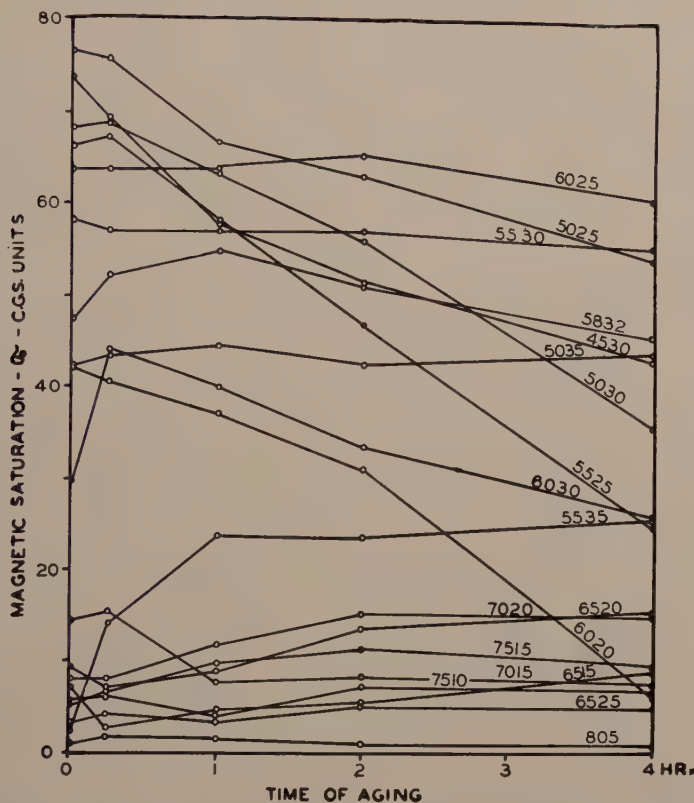


FIG. 4.—EFFECT OF AGING AT 200°C. ON MAGNETIC SATURATION MOMENT OF RAPIDLY QUENCHED BETA ALLOYS.

First two figures on each curve designate atomic per cent of copper and others that of manganese.

about 12,000 oersteds, which proved to be ample to saturate the powders.

Measurements were made at room temperature and at a very low temperature. The low-temperature measurement was made by suspending the specimen within a small glass tube inserted in liquid nitrogen. The saturation value at this temperature is not detectably different from that at absolute zero for substances with a Curie point above room temperature. Repeated measurements gave results that checked one another within 2 per cent. The results

same composition and heat-treatment. A possible cause for this is the more rapid cooling experienced by powders during a quench. This was confirmed by the fact that the powders were more magnetic when quenched in boiling water.

Samples were then aged at 200°C. for varying periods of time. The results for rapidly quenched specimens are shown in Fig. 4. In general, there seems to be an initial increase in magnetizability, followed by a decrease, like hardness curves in age-hardening. In some samples, the initial

increase is not apparent; in others, the decreasing stage has not been reached. X-ray diffraction patterns show no change during the period of increase but show that decomposition into other phases occurs during the decrease. Contours of maximum

ture an increase in the degree of order occurs that is sufficient to affect the magnetizability. As time passes, the diffusion processes necessary for decomposition take place and nonmagnetic phases are formed, causing the decrease in magnetizability.

TABLE I.—*Magnetic Saturation Values for Quenched and Aged Beta Alloys*

Atomic Per Cent			Annealing Temperature, Deg. C.	As Quenched		After Aging at 200°C.							
						A		B		C		D	
Cu	Mn	Sn		R	S	R	S	R	S	R	S	R	S
At 25°C.													
85	0	15	650	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
80	5	15	715	0.52	0.51	0.63	0.46	0.52	1.09	0.66	0.69	0.43	0.09
75	15	10	715	0.49	0.73	0.66	0.78	2.71	2.20	3.17	2.53	2.48	2.52
75	10	15	715	2.23	0.95	2.23	0.56	1.82	1.54	3.54	1.38	2.72	1.12
70	20	10	640	1.09	9.54	1.54	9.84	5.22	10.30	6.87	10.86	7.03	11.56
70	15	15	680	0.88	0.37	0.99	0.59	1.62	0.26	1.62	0.37	1.19	0.65
65	25	10	640	0.39	2.33	1.25	2.85	0.58	0.60	1.06	2.68	0.82	2.16
65	20	15	640	1.62	1.22	1.50	1.48	3.49	2.82	6.30	6.30	7.90	9.22
65	15	20	640	1.82	1.58	1.29	1.25	3.02	2.61	4.34	4.43	7.19	6.05
60	30	10	640	21.79	24.60	28.60	32.00	27.54	30.08	24.35	27.38	19.22	22.50
60	25	15	650	54.00	11.72	53.88	11.44	53.70	12.21	53.93	12.21	50.15	12.17
60	20	20	650	35.85	36.73	35.18	36.23	32.78	33.90	26.83	30.45	11.34	19.39
58	32	10	650	39.55	39.05	42.20	40.00	43.85	40.50	41.95	38.70	36.50	33.63
55	35	10	640	1.50	2.74	12.38	13.32	20.53	20.75	21.59	22.09	21.80	22.68
55	30	15	640	49.53	28.43	49.10	28.30	49.10	28.43	49.23	28.23	46.90	26.80
55	25	20	650	57.05	50.80	57.20	50.15	49.60	46.40	40.25	43.15	18.21	31.80
50	35	15	640	38.08	41.15	38.45	41.65	39.25	40.55	38.65	41.05	36.90	38.35
50	30	20	640	61.35	61.10	61.35	61.45	54.85	53.90	49.60	47.90	28.23	26.45
50	25	25	640	69.60	68.05	68.65	66.00	60.35	58.95	57.25	55.65	48.90	48.70
45	30	25	640	67.10	64.40	63.45	60.30	52.45	52.60	46.40	49.15	39.40	43.70
At Liquid Nitrogen Temperature													
85	0	15	650	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
80	5	15	715	1.00	0.93	1.18	0.93	1.12	1.36	0.81	0.81	0.75	0.47
75	15	10	715	5.08	4.68	6.62	7.05	9.90	8.71	10.15	9.29	9.32	9.17
75	10	15	715	5.44	3.53	5.62	4.29	3.66	4.78	6.69	5.07	5.86	4.64
70	20	10	640	8.15	19.26	8.15	19.31	11.73	18.39	15.10	20.70	14.99	21.90
70	15	15	680	14.10	1.10	15.28	1.21	7.99	0.79	8.17	0.82	6.98	1.18
65	25	10	640	3.99	9.22	3.94	3.89	3.34	2.16	5.52	3.71	4.90	4.24
65	20	15	640	9.64	9.22	7.71	8.71	9.04	10.52	13.82	14.38	15.06	17.16
65	15	20	640	7.22	4.51	2.79	2.79	4.28	3.83	5.33	6.11	9.91	8.48
60	30	10	640	29.92	33.55	43.78	46.65	40.00	42.00	33.16	37.70	26.08	30.30
60	25	15	650	63.50	24.00	63.55	24.25	63.35	24.83	65.05	24.55	60.70	24.80
60	20	20	650	42.05	42.15	40.80	41.55	37.40	38.58	30.78	34.73	10.32	23.75
58	32	10	650	47.88	48.00	52.25	49.80	55.05	52.00	51.05	48.30	45.40	42.00
55	35	10	640	2.24	3.24	14.10	15.12	23.75	24.13	23.35	24.60	25.05	25.30
55	30	15	640	58.45	38.75	57.05	37.90	57.35	38.30	57.30	36.60	55.75	36.77
55	25	20	650	66.35	58.90	67.15	58.45	58.30	53.75	46.85	49.65	25.45	36.80
50	35	15	640	42.30	45.75	43.50	47.20	44.40	46.70	42.40	45.10	43.05	45.35
50	30	20	640	68.75	69.00	69.20	70.35	63.15	62.50	56.20	53.70	35.40	32.90
50	25	25	640	76.05	74.90	75.90	72.80	66.55	65.45	62.90	63.05	54.05	53.70
45	30	25	640	74.00	71.55	69.00	66.45	57.90	58.80	51.50	54.75	42.75	54.70

R, specimens quenched initially in cold water from the beta range.

S, specimens quenched initially in boiling water from the beta range.

A, specimen aged for $\frac{1}{4}$ hr and quenched.

B, same specimen aged $\frac{3}{4}$ hr. more and quenched again.

C, same specimen aged 1 hr. more and quenched again.

D, same specimen aged 2 hr. more and quenched again.

magnetization for beta copper-manganese-tin samples are given in Fig. 5.

The cause of the initial increase is not clear, but it is possible that at this tempera-

Filings taken from a magnetic ingot were found to have largely lost their magnetism. However, the magnetism could be restored partly by aging at 200°C., or completely by

annealing in the beta range and quenching. This also supports the ordering explanation. Dehlinger and Graf²³ and others have observed that superlattice lines disappear

tion may well be of the type observed microscopically in beta copper-zinc alloys, and suggested in beta copper-tin alloys by Greninger and Mooradian,²⁶ since mar-

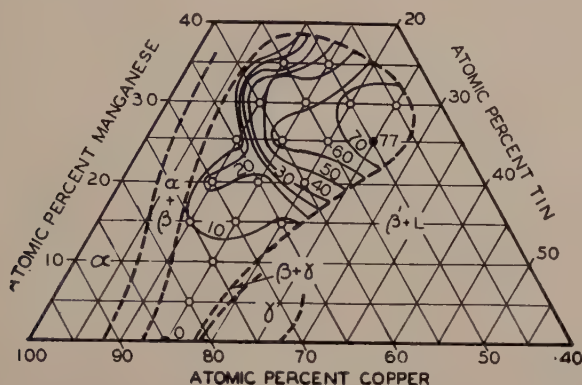


FIG. 5.—CONTOURS OF MAXIMUM MAGNETIC SATURATION MOMENT OF BETA COPPER-MANGANESE-TIN ALLOYS.

on deformation, and it is generally accepted that cold-work destroys order. Dahl²⁴ observed that Ni_3Mn , which is supposed to be ordered, lost most of its magnetism on severe deformation. It is probable therefore that in this case the drastic cold-work of filing has destroyed the ordering, resulting in loss of ferromagnetism, and the ordering is partly restored on aging at 200°C .

Evidence of a reversible low-temperature transformation was found in a sliver of the approximate composition $\text{Cu}_{11}\text{Mn}_7\text{Sn}_2$. A sample that had been aged for 15 min. at 200°C . was immersed in liquid nitrogen, and a considerable decrease in magnetization, perhaps 15 per cent, was experienced at approximately minus 160° to minus 180°C ., reversing on heating at minus 120° to minus 150°C . This behavior was confined to the aged sliver; the original quenched sliver behaved normally. Aging, however, produced no appreciable increase in magnetizability, indicating the presence of a high degree of ordering in the sliver. Powders of the same composition subjected to a similar treatment did not exhibit this anomalous behavior. Apparently specimen size is an important factor. The transforma-

tion may well be of the type observed microscopically in beta copper-zinc alloys, and suggested in beta copper-tin alloys by Greninger and Mooradian,²⁶ since mar-

DISCUSSION OF RESULTS

Ferromagnetism is considered to arise from the mutual interaction of elements with incomplete inner shells of electrons.²⁶ Transition metals (including the rare earths) are the only ones that have these shells. Slater²⁷ has found theoretically that the interaction is effective only when the distance between the atoms is more than 1.5 times the diameter of the incomplete inner shells. A maximum of one Bohr magneton per unpaired electron in the incomplete shell is to be expected, but usually there is less. Thus, the saturation value of iron is 2.2 Bohr units per atom, compared with a theoretical 3, cobalt 1.7 out of 2, and nickel 0.6 out of 1.

Manganese is the only transition element in the Heusler alloys and the ferromagnetism is often ascribed to it, especially since certain binary alloys of manganese with

arsenic, bismuth, boron, carbon, hydrogen, nitrogen, phosphorus, sulphur, antimony, selenium, silicon and tin have been reported to be ferromagnetic.²⁸ In the present research, the unusually high value of 4.14 Bohr magnetons per atom of manganese has been found (Table 2). This is much higher than any previously reported values.²⁹ If all this comes from the manganese, it would be necessary for at least some of the atoms to have a moment of 5, which requires two electrons to be in the outer shell; the manganese would then be divalent. Even so, the value is larger than would be expected from the value for iron just mentioned.

TABLE 2.—*Number of Bohr Magnetons per Atom of Manganese in Beta Copper-manganese-tin Alloys*

Atomic Per Cent			σ_0 (Maximum)	Bohr Magnetons
Cu	Mn	Sn		
85	0	15	0.00	0.00
80	5	15	1.36	0.35
75	15	10	10.15	0.83
75	10	15	6.69	0.85
70	20	10	21.90	1.33
70	15	15	15.28	1.29
65	25	10	5.52	0.27
65	20	15	17.16	1.08
65	15	20	9.91	0.87
60 ^a	30	10	46.65	1.85
60 ^a	25	15	65.05	3.26
60 ^a	20	20	42.15	2.76
58 ^a	32	10	55.05	2.05
55 ^a	35	10	25.65	0.87
55 ^a	30	15	58.45	2.42
55 ^a	25	20	67.15	3.50
50 ^a	35	15	47.20	1.67
50 ^a	30	20	70.35	3.04
50 ^a	25	25	76.65	4.14
45 ^a	30	25	74.00	3.31

^a Highly ordered alloys.

An alternative, which finds some favor,^{27,30} is that the copper is divalent, leaving one empty place so that copper acts as a transition metal. This is supported by the fact that in chemical compounds copper often is divalent. Also, it appears to some investigators that the manganese atoms are too far apart in the Heusler alloy for effective magnetic interaction.

The present investigation cannot solve these problems, but the value of magnetic

saturation, which is about one Bohr magneton per manganese atom higher than any previously reported, should have a bearing on any theoretical work.

The beta phase has been found to have a considerable range of existence. If we assign usual valences³¹ to the atoms (one for copper, four for tin, and zero for manganese), the maximum number of valence electrons per atom would be near 1.5, as predicted by the Hume-Rothery rule.³² However, as just shown, the valences of either copper or manganese must be higher, so that further conflicts are raised.

Superlattice lines were observed in X-ray photograms of all highly magnetic alloys. The other beta alloys were either not ferromagnetic or were only weakly so. The presence of local ordering cannot be excluded in these. Therefore it seems that ordering is closely related to ferromagnetism, and may be necessary for it. Observations made on beta alloys by varying quenching velocities, plastic deformation, and aging experiments also suggest that ordering promotes high saturation values.

Only one maximum of ferromagnetism was found in the beta phase of this system. The second one, at $\text{Cu}_6\text{Mn}_3\text{Sn}$, reported by F. Heusler and by Take and Semm, was found qualitatively in cast alloys. However, when higher magnetizability was produced by suitable heat-treatment, this was no longer a maximum. The maximum observed in this investigation occurs in the ideally ordered alloy Cu_2MnSn , and has a value of $\sigma_0 = 76.65$ ergs per gauss per gram ($I_0 = 660$). This value is the highest ever found in any of the Heusler alloys and exceeds that of nickel by 30 per cent.

SUMMARY

A systematic investigation of the ferromagnetic nature of the copper-manganese-tin system has been made. X-ray, microscopic and magnetometric methods were extensively employed. Only the beta phase of the system was found to be magnetic.

The region of existence of this phase has been partly outlined and found to extend over a considerable range of composition at varying temperatures above 625°C. There exists also a close agreement between the phase boundary and the Hume-Rothery rule when usual valences are assigned to the elements.

Beta alloys containing more than 20 atomic per cent manganese were found by X-ray diffraction methods to have long-range ordering. Ordered alloys were generally brittle. The distribution of atoms within the superlattice at the composition Cu_2MnSn was established by special X-ray diffraction techniques. A high-temperature X-ray photogram showed the alloy to be ordered at 630°C.

A quantitative magnetometric analysis of beta copper-manganese-tin alloys was made at both room temperature and near the temperature of liquid nitrogen. These indicated that high magnetizabilities were confined to alloys having long-range ordering. That ferromagnetism and ordering are related was shown by varying quenching velocities, by plastic deformation, and by aging experiments performed on beta alloys.

The maximum of ferromagnetism for the system occurs at the ideally ordered composition Cu_2MnSn with a magnetic saturation moment of $\sigma_0 = 76.65$ ergs per gauss per gram (or $I_0 = 660$), the highest value reported for any of the Heusler alloys. The second maximum found by early investigators at the composition $\text{Cu}_6\text{Mn}_3\text{Sn}$ was found qualitatively in cast alloys, but did not exist in the more strongly magnetic alloys that had been properly heat-treated.

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DISCUSSION

(Edmund M. Wise presiding)

H. FRIEDMAN,* Anacostia, Washington, D. C.—As pointed out by Dr. Carapella, the high value of saturation magnetic moment found for one of his Heusler alloys has an interesting bearing on the theory of the magnetic properties of Heusler alloys. Slater's²⁷ suggestion that copper is partially ionized in the d shell when alloyed with manganese seems to be the most plausible explanation. If all the magnetism is attributed to manganese, an extremely improbable value of 4.14 Bohr magnetrons per atom is obtained from the experimental data. If, however, copper contributes in part to the magnetic moment, a reasonable value, much closer to 2 Bohr magnetrons per atom, may be obtained. The

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following is a suggested experimental attack on the problem of determining whether copper is magnetic in the Heusler alloy.

Free atom spectroscopy gives the electronic energy levels of free atoms. Analogously, X-ray spectra of solids give information about the electronic energy levels of solids. In particular, the KB_2 and KB_5 lines of the first transition group elements have shapes that reflect the distribution of electrons in the $3d$ and $4s$ levels of the solid. A number of brasses, copper-nickel alloys and zinc-nickel alloys have been studied by the X-ray method.³³⁻³⁵ The alloy sample is used as the target in an X-ray tube and the characteristic radiation is analyzed by a double crystal spectrometer and Geiger counter intensity-measuring device.

By analysis of the shapes of the KB_2 and KB_5 lines of these alloys, it was possible to deduce semiquantitatively the electron-energy distributions. The results were in agreement with the theoretical interpretations of magnetic properties, electrical resistance, superlattice energies, etc. The X-ray line from copper has a very characteristic shape, which makes it simple to follow any slight changes accompanying alloying. By studying the shape of the copper emission from the Heusler alloy, and comparing it with the same lines from pure copper and other 50 per cent copper alloys, it should be possible to determine whether or not copper is ionized in the d shell when alloyed with manganese.

L. A. CARAPPELLA (author's reply).—How the "magnetic electrons" are distributed in

these ferromagnetic alloys has indeed been the subject of much consideration, owing largely to the fact that the alloying elements are in themselves nonmagnetic. Several speculations have been advanced, but, as it has been mentioned here and in a previous publication,³⁶ they appear a bit conflicting on the basis of the results of this research. The suggestion of studying certain characteristic emissions from X-ray spectra of these alloys by the double crystal spectrometer and Geiger-Müller counter technique seems to be a direct approach to the problem, and may yield the information that now is lacking.

However, in using the experimental technique described above (in which the alloy serves as the target of an X-ray tube), care must be taken to provide sufficient cooling for the target material, or it will tend to decompose to a nonmagnetic state. The magnetic phase, as shown by this work, is relatively unstable below 625°C . The possibility of operating the X-ray tube in such a manner that the temperature of the target is above 625°C . (i.e., in a temperature range where the material is stable) will avoid decomposition, but will introduce an undesirable factor because the alloys at these temperatures are nonmagnetic, owing to their low "Curie points of magnetism." The state of the "magnetic electrons" in the system obviously is altered under this condition, and, consequently, the results thus obtained will be rendered inadequate. These represent a few precautions that must be borne in mind in employing the suggested experimental technique, because of the nature of these ferromagnetic alloys.

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³⁶ L. A. Carapella and R. R. Hultgren: *Phys. Rev.* (1941) **59**, 905.

Some Mechanical Properties of Manganese-copper Alloys

BY ALFRED H. HESSE,* JUNIOR MEMBER A.I.M.E., AND EDWIN T. MYSKOWSKI*

(New York Meeting, February 1942)

THE development by the U. S. Bureau of Mines of a process for purifying manganese by electrolysis has stimulated interest in manganese alloys. While recent publications have shown some alloys of manganese and copper to possess rather unusual properties, none have included information on tensile properties, which have an important bearing on the usefulness of the alloys.

Manganese-copper alloys can be heat-treated, since the single phases that exist at high temperatures may be retained by quenching. According to Persson,¹ when quenched alloys containing from about 30 to nearly 100 per cent manganese are reheated, alpha manganese is precipitated (Fig. 1). Calculations based on Persson's X-ray data indicate that this decomposition is accompanied by a change in volume of as much as 5 per cent. The reason that this large volume change has not been noted probably is the slow rate at which equilibrium is reached by these alloys.

In an investigation on hardening by cold-work and heat-treatment, Dean and Anderson³ found that quenched alloys increase in hardness with manganese content and that high-manganese alloys harden very slowly with cold-work, while high-copper alloys harden much more rapidly. Heat-treatment has little effect on manganese-copper alloys containing less than

40 per cent Mn, and affects those alloys containing more than 40 per cent in accordance with their manganese content and heat-treating temperature. Dean and Anderson⁴ also found that cold-work increased electrical resistance of alloys containing from 50 to 80 per cent Mn, and that heat-treatment of alloys containing from 40 to 96 per cent Mn altered the electrical resistance considerably. Dean, Anderson and Potter⁵ have shown that the high vibration damping capacity that characterizes manganese-copper alloys containing 40 to 90 per cent Mn is affected by cold-work and heat-treatments. Highest vibration damping capacity at low stresses was obtained by heating for 2 hr. at 450°C. (842°F.) after quenching from solution temperatures.

Preparation of Alloys.—The alloys for these tests were melted in a 17-lb. basic-lined high-frequency induction furnace using electrolytic manganese, grade A ingot copper and a 70-30 Cu-Mn master alloy (69.80 per cent Cu, 0.12 Fe, 0.04 Si, 0.006 S, 0.07 C, balance Mn). The manganese was heated slowly to expel excess dissolved gases and melted before the addition of copper. No fluxes or covers were used. The melts were cast in tapered iron molds and the ingots were reduced 90 per cent when forged to 1/2-in. rounds. These rods were given 2-hr. solution treatments at temperatures that depended upon the composition (Table 1).

Tensile Tests.—The tensile specimens, 0.313-in. diameter (1.25-in. gauge length),

Published by permission of the Navy Department. Manuscript received at the office of the Institute Dec. 1, 1941. Issued as T.P. 1446 in METALS TECHNOLOGY, April 1942.

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¹ References are at the end of the paper.

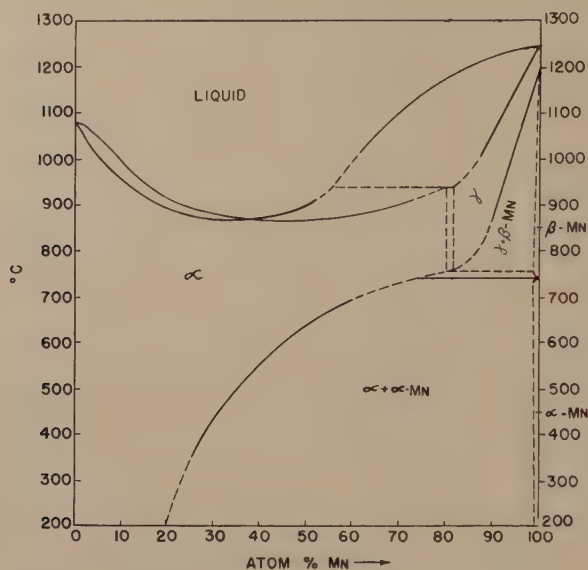


FIG. 1.—COPPER-MANGANESE DIAGRAM (PERSSON, 1930).

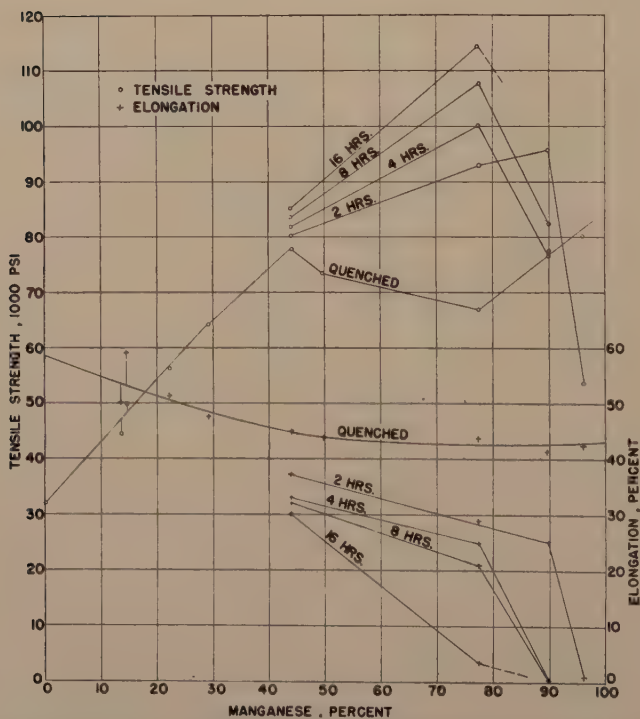


FIG. 2.—TENSILE STRENGTH AND ELONGATION OF MANGANESE-COPPER ALLOYS AS QUENCHED AND AS TEMPERED AT 450°C. (842°F.).

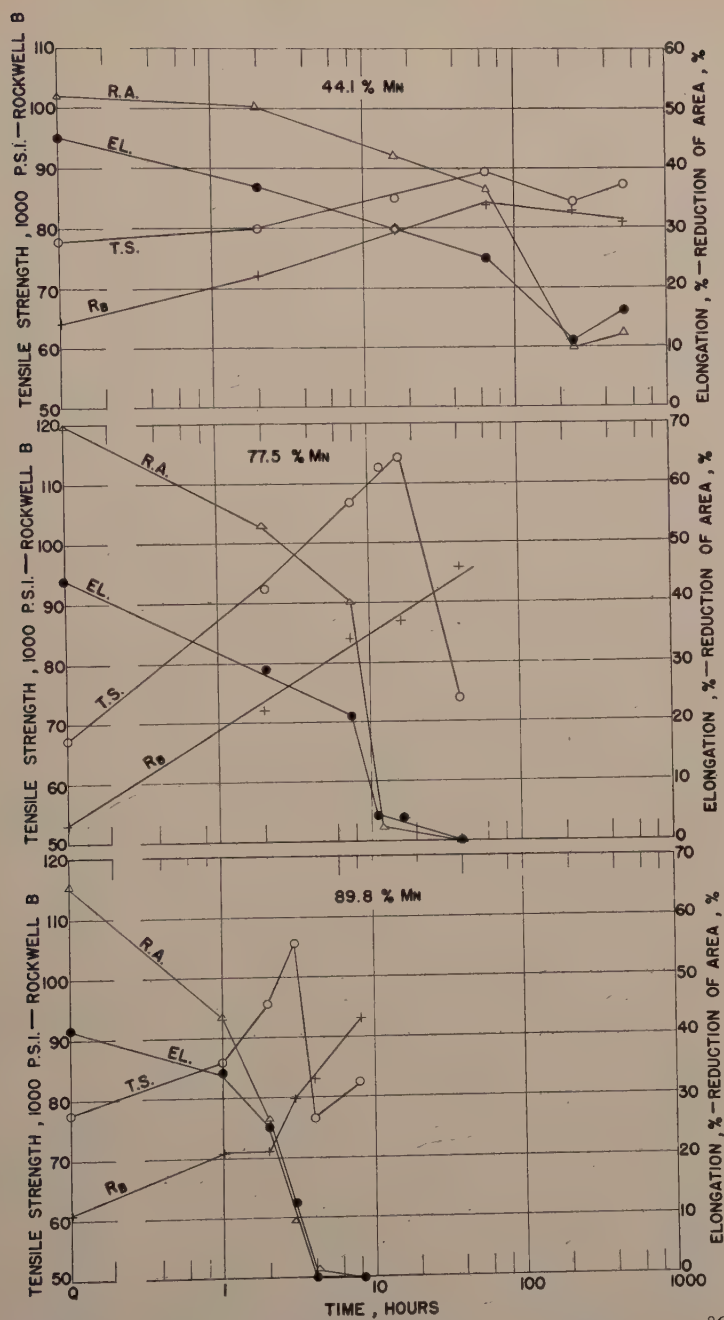


FIG. 3.—PROPERTIES OF SOME ALLOYS AS QUENCHED (*Q*) AND AS TEMPERED AT 450°C. (842°F.).

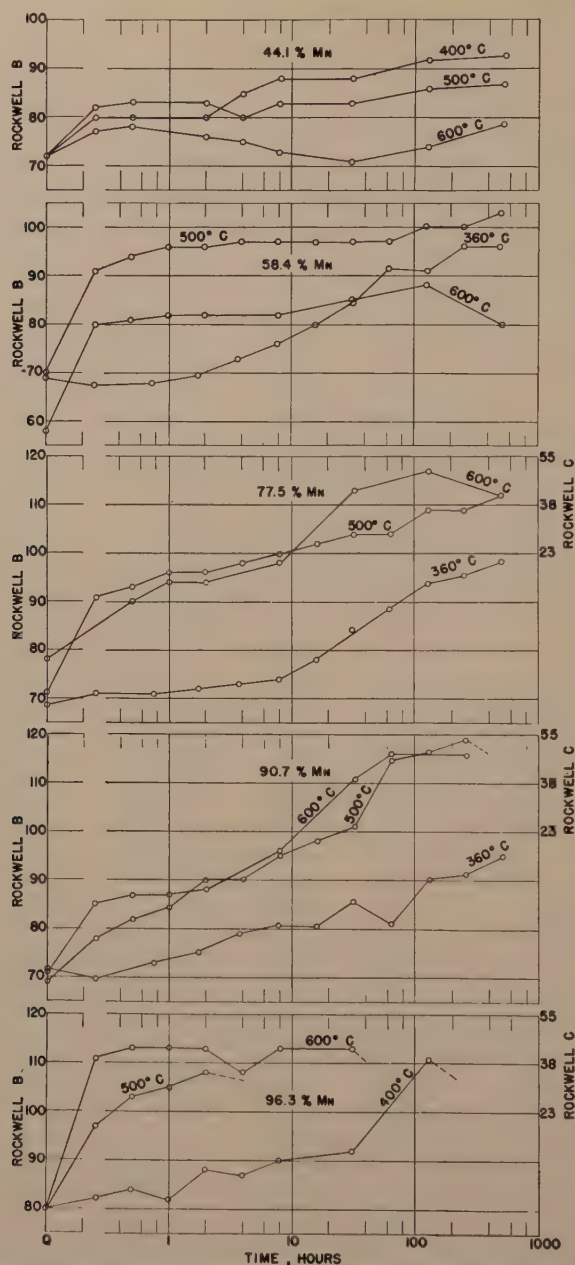


FIG. 4.—HARDNESS OF SOME MANGANESE-COPPER ALLOYS AS QUENCHED (Q) AND AS TEMPERED.

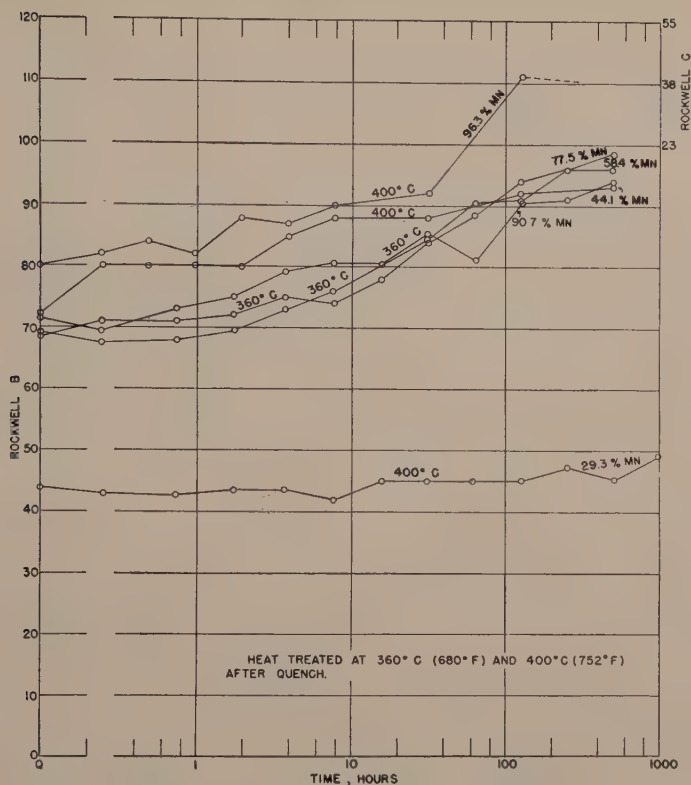


FIG. 5.—HARDENING MANGANESE-COPPER ALLOYS AFTER QUENCHING.

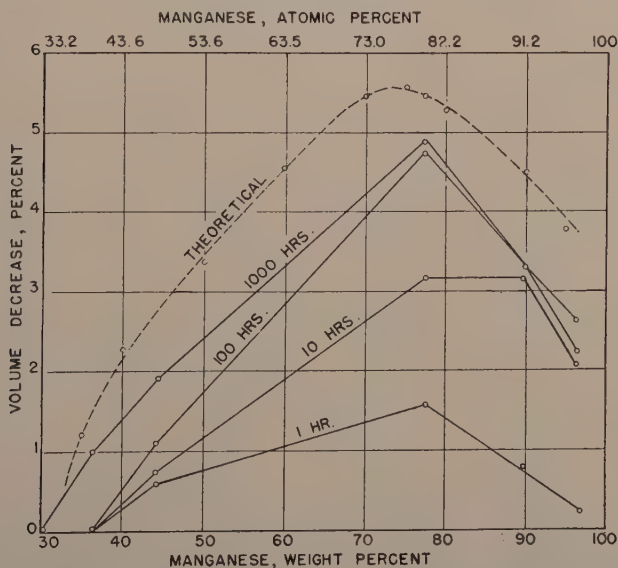


FIG. 6.—EFFECT OF TEMPERING ON VOLUME CHANGE OF MANGANESE-COPPER ALLOYS AFTER QUENCHING.

$$T = 500^{\circ}\text{C. } (932^{\circ}\text{F.})$$

which were enclosed in evacuated Pyrex containers, were tempered at 450°C. (842°F.). The response of the manganese-copper alloys to heat-treatment is in accord with their constitution. Tensile strength and hardness increased with time, while the ductility decreases (Figs. 2 and 3).^{*} However, as the ductility of the high-manganese alloys becomes very low, the observed tensile strength also decreases. This behavior is not surprising, since relatively large amounts of the hardening phase, alpha manganese, are involved. The data include tests made after the heat-treatment found to produce the highest damping capacity;⁴ namely, 2 hr. at 450°C.

TABLE I.—Alloys Tested

Heat No.	Composition, Per Cent		Quenching Temperature, Deg. C.
	Mn	Cu	
44	13.6	85.7	750
49	14.5	85.4	750
50	22.1	77.7	750
51	29.3	70.4	750
79	36.3	63.6	750
86	44.1	55.9	750
54	58.4	41.4	800
55	77.5	22.4	800
56	90.7	9.0	1000
87a		10.2	1000
88a		3.7	1100

Hardness.—The change in hardness with time at temperature (Figs. 4 and 5)^{*} is of interest because the 44.1 per cent Mn alloy contains just enough manganese to harden below 600°C. by precipitating sufficient alpha manganese, while the 96.3 per cent alloy precipitates with time a large amount of hard, brittle alpha manganese cemented together with a small amount of the ductile copper solid solution. Several specimens became so brittle that it was impossible to determine the hardness. This is indicated in Figs. 4 and 5 by a descending broken line.

Volume Change.—Since data such as those on the change of hardness with time at temperature indicate that the rate of reaction of manganese-copper alloys is very

slow, an attempt was made to follow the precipitation of alpha manganese by careful density measurements. The specimens for these determinations were machined cylinders with a volume of 0.11 cu. in., one for each tempering time. The density of each specimen was determined at 20°C. \pm 1°C. before and after heat-treatment, with an observed accuracy of \pm 0.3 per cent. The specimens were enclosed in evacuated Pyrex containers for protection during heat-treatment.

For comparison with the observed volume change, a curve is shown (Fig. 6) that gives the change to be expected from Persson's X-ray data.

CONCLUSIONS

Manganese-copper alloys possess an excellent combination of tensile strength and ductility. However, if the high-manganese alloys are held at temperature too long, the ductility suffers.

Manganese-copper alloys were found to have slow rates of reaction. This is not inconsistent with the complex structure of alpha manganese and its low solubility for copper.

ACKNOWLEDGMENT

The authors wish to express their appreciation to the Navy Department for permission to publish this work.

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^{*} Mn is plotted in weight per cent.

DISCUSSION

(C. S. Barrett *presiding*)

C. S. SMITH.—Have the authors any data on the yield strengths as well as the tensile strengths?

A. H. HESSE (author's reply).—We determined yield strength for several compositions at various heat-treatments. The stress corresponding to a 0.2 per cent gauge length offset from the modulus slope was considered the yield strength, which coupled with tensile strength is given in Table 2. The tempering temperature was 450°C. (842°F.). In some cases the yield strength appears to be quite high.

TABLE 2.—*Yield Strength*

Heat No.	Tempering Time, Hr.	Yield Strength, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.
51	As quenched 38	33,800 32,500	64,200 62,900
86	As quenched 2 240	48,700 54,700 74,400	77,900 80,200 84,500
55	2 8	80,100 91,400	92,900 107,100
87a	2 3	79,400 81,700	95,800 105,600

Relief of Residual Stress in Some Aluminum Alloys

BY L. W. KEMPF* AND K. R. VAN HORN,* MEMBERS A.I.M.E.

(Philadelphia Meeting, October 1941)

PLASTIC deformation of most commercial metals within a sufficiently low temperature range results in profound changes in structure and properties, of which the causes and effects are not completely understood. One of these effects is the presence of internal residual stresses and strains, which ordinarily do not appear to require specific consideration in most structural applications but which may be quite undesirable in particular instances. For example, in heavy sections that require considerable machining before assembly, residual stresses may be undesirable because of the distortion they cause when their balance is disturbed by machining or otherwise. In addition, the distribution of stresses may be such that it acts in the same direction as the applied load, thus bringing about premature failure or reducing the load-carrying capacity of the member.

One source of residual stress in metal structures is the plastic deformation that may occur during rapid cooling from relatively elevated temperatures, as in the cooling of a casting in the mold or the quenching of a heavy section from elevated temperatures during heat-treatment. These residual stresses are usually undesirable because their direction of operation and magnitude cannot be controlled well enough to permit utilization of the changes in properties of the metal that they may bring about. The most convenient manner of controlling such residual stress is by proper selection of the cooling rate or by

reheating to a temperature at which plastic flow can take place, resulting in relief of the residual stresses and strains. Both of these methods of control, however, may cause a reduction in the optimum properties obtainable from the previous operation. A compromise must be struck, and if it is to result in the best possible combinations of properties, specific information must be available regarding the magnitude of the stresses and the rate at which they are affected by variations in cooling rate or in reheating temperature.

The complete quantitative estimation of residual stress in complicated metal shapes is exceedingly difficult, if not impossible. In simple sections, however, relatively quantitative analysis may be applied and useful estimations of stress distribution may be made. This paper is concerned largely with the rate of relief, upon reheating, of internal residual stress in simple aluminum-alloy structures. Since even with simple structures quantitative estimation of residual stresses is laborious and costly, an attempt was made to find other means of collecting data upon which commercial heat-treatments might be based. Incidentally, a few data were collected bearing on the problem of relaxation of aluminum alloys.

DETERMINATION OF RESIDUAL STRESSES

The magnitude and distribution of residual stresses in simple aluminum-alloy shapes rapidly cooled from elevated temperatures has been discussed in a previous paper.¹ Fig. 1 reproduces some of the data

Manuscript received at the office of the Institute Jan. 9, 1941. Issued as T.P. 1334 in METALS TECHNOLOGY, June 1941.

* Aluminum Research Laboratories, Aluminum Co. of America, Cleveland, Ohio.

¹ References are at the end of the paper.

from that paper and indicates the profound influence of quenching conditions on the magnitude of residual stress.

The diagrams of Fig. 1 differ somewhat from the diagrams in the original paper. This difference is the result of a different treatment of the data in the deduction of the most probable stress distribution. The original Sachs² equations for the calculation of residual stresses in cylinders are:

Longitudinal Stress:

$$S_L = \frac{E}{1 - \gamma^2} \left[(F_b - F) \frac{\Delta(\alpha + \gamma\beta)}{\Delta F} - (\alpha - \gamma\beta) \right]$$

Tangential Stress:

$$S_T = \frac{E}{1 - \gamma^2} \left[(F_b - F) \frac{\Delta(\beta + \gamma\alpha)}{\Delta F} - \frac{F_b + F}{2F} (\beta + \gamma\alpha) \right]$$

Radial Stress:

$$S_R = \frac{E}{1 - \gamma^2} \left[\frac{F_b - F}{2F} (\beta + \gamma\alpha) \right]$$

where Δ = differential sign,
 E = modulus of elasticity,
 γ = Poisson's ratio,
 F_b = complete cross section of undrilled cylinder,
 F = drilled-out cross section,
 ΔF = cross section of one drilled layer,
 α = unit length change,
 β = unit diameter change.

If this equation is solved for each individual set of measurements and the results plotted, a diagram results such as appears in the preceding paper. However, the functions $(\alpha + \gamma\beta)$ and $(\beta + \gamma\alpha)$, which represent the dimensional changes in length and diameter, may be plotted against the drilled-out cross section of the cylinder. Usually a straight line or a smooth curve may be drawn to represent this relationship. If a straight line is obtained, the slope of this line represents the function $\frac{\Delta(\alpha + \gamma\beta)}{\Delta F}$ or $\frac{\Delta(\beta + \gamma\alpha)}{\Delta F}$. If a curve is obtained, its slope may be determined readily at any desired point and the above

functions so obtained. Values from this curve or line are used in the original equations for the calculation of stress. In this manner the measured values are equalized, and any error in measurement or calculation can be readily detected. Interpolation and extrapolation may then be carried out with a greater degree of probability. This method of treatment is now usually used in the application of the Sachs method of stress analysis.

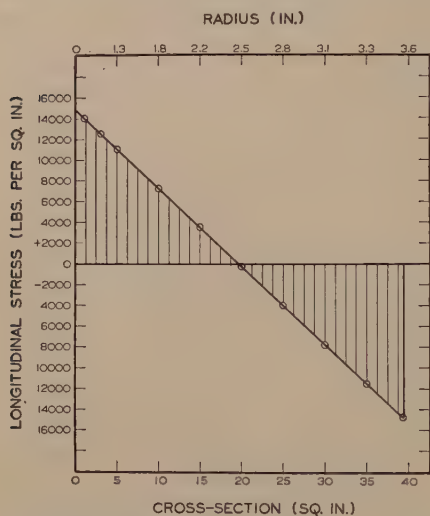
The procedure utilized in applying the Sachs method to the determination of residual stress in solid cylinders and tubing in this investigation was as follows: The solid cylinders were usually about .7 in. long by .7 in. in diameter. The circumferential surfaces were machined and ground to a finish, which permitted measurement to ± 0.0001 in. The bases were finished by polishing with French emery paper on a base plate. To ensure successive measurements being made at fixed points, reference marks were inscribed on one base of each of the cylinders. The solid cylinders were then annealed to remove the residual stresses derived from the previous fabrication or the machining operation. Annealing treatments consisted of 9 hr. heating to 345°C. (650°F.), 1½ hr. at temperature, and then 36 hr. cooling to 95°C. (200°F.) in the furnace.

For the stress analysis of extruded or drawn tubing, cylinders were cut approximately to length and then machined to the desired dimensions. It was necessary to take a light cut from the outside diameter in order to obtain a tube exactly circular and also to improve the surface for accurate measurements.

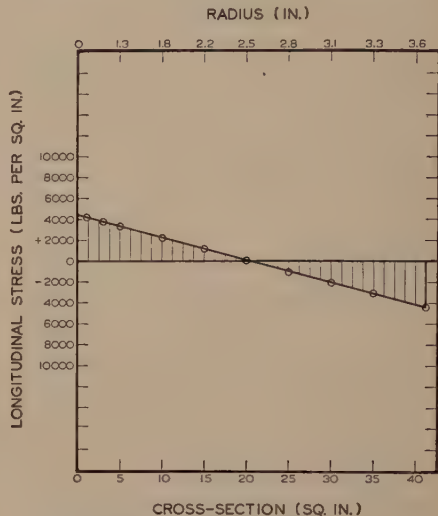
After the desired heat-treatments, the cylinders were measured on a Federal Comparator, using standardized gauge blocks for reference. Ten locations on each cylinder were measured, four on the base (length measurements) at 90° intervals on a circle of 6½-in. diameter and six on the circumference (diameter measurements).

The circumference positions were on two elements of the cylinder, 90° to each other, and located 1 in., $3\frac{1}{2}$ in., and 6 in. from the reference base. The measuring procedure

were measured. The circumference positions were located on two elements of the cylinders at 90° to each other, 1 in. from either base and in the center of the element.



a. Cylinder quenched from $540^\circ\text{C. (1000}^\circ\text{F.)}$ in cold water.



b. Cylinder quenched from $540^\circ\text{C. (1000}^\circ\text{F.)}$ in boiling water.

FIG. 1.—DISTRIBUTION OF RESIDUAL STRESS IN SOLID 51S ALLOY CYLINDERS.
Alloy 1 per cent Si, 0.6 per cent Mg, balance Al.

was to place the cylinder in a constant-temperature $21^\circ\text{C. (70}^\circ\text{F.)}$ liquid bath for 2 hr., then three measurements were made for each of the 10 locations and the cylinder was returned to the bath for at least one additional hour. After this period, the locations were measured twice. An attempt was made to maintain measuring temperature at $21^\circ\text{C. (70}^\circ\text{F.)}$, but variations were noted and when necessary the measurements were corrected accordingly. The dimensions were measured to 0.0001 in. and estimated to 0.00005 inch.

The cores of the solid cylinders were bored out in separate operations, so that the inside diameter was successively 1 in., 2 in., 3 in., 4 in., 5 in. and 6 in. within ± 0.001 in. Care was exercised in the boring operation to prevent distortion of the cylinders. The 10 locations were remeasured after each boring operation.

Similarly, in tubing, four locations at 90° on the base and six on the circumference

The specimens were measured at the points indicated, according to the procedure described for solid cylinders. Approximately $\frac{1}{16}$ -in. cuts were removed from the inside wall of each cylinder between measurements.

RATE OF RELIEF OF RESIDUAL STRESS BY REHEATING AS DETERMINED BY THE SACHS METHOD

To ensure proper selection of conditions for obtaining optimum combinations of mechanical properties, resistance to corrosion, volumetric stability, and freedom from residual stress in heat-treated aluminum alloys, it appeared desirable to obtain some data on the rate of relief of residual stress. In one experiment a series of sand-cast and machined 122 alloy (10 per cent Cu, 1.25 Fe, 0.25 Mg, balance Al) right cylinders 6 in. in diameter by 6 in. long were quenched in water at $12^\circ\text{C. (55}^\circ\text{F.)}$

after heating for 16 hr. at 480°C . (895°F .). It was planned to determine the magnitude of the residual stresses in the as-quenched condition, and after heating for various

from this that the initial residual stress in these cylinders was near the tensile strength of the alloy. The diagrams of Fig. 2 give the magnitude and distribution of the stresses

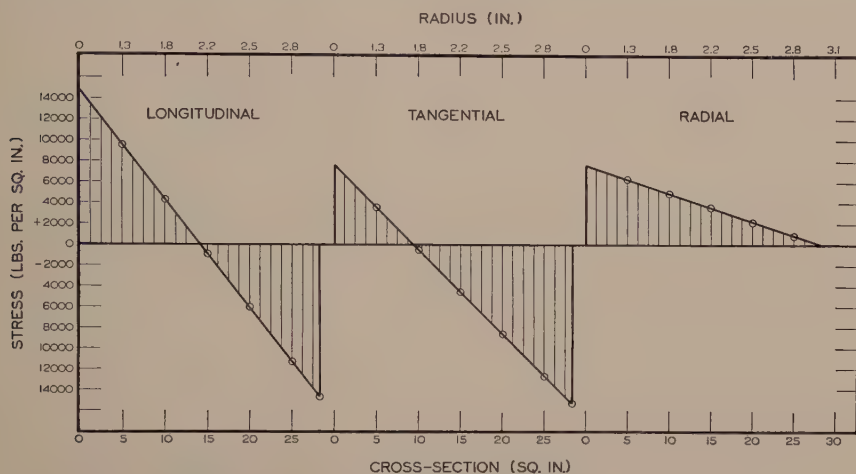


FIG. 2.—DISTRIBUTION OF RESIDUAL STRESSES IN SOLID 122 ALLOY CYLINDER.

Alloy 10 per cent Cu, 1.2 per cent Fe, 0.2 per cent Mg, balance Al. Heat-treated 16 hr. at 480°C . (895°F .), quenched in cold water and annealed 3 hr. at 225°C . (435°F .).

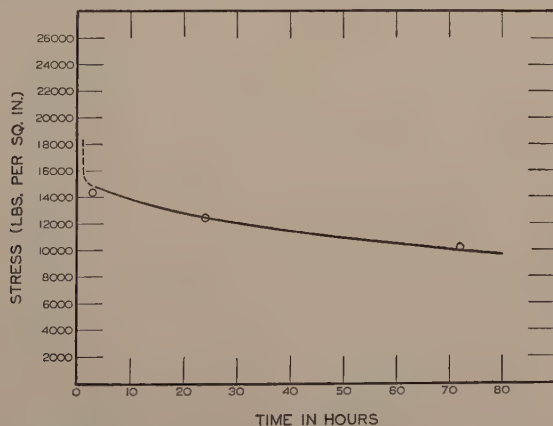


FIG. 3.—RELIEF OF TANGENTIAL RESIDUAL STRESS AT 225°C . (435°F .) IN SOLID 122 ALLOY CYLINDERS.

Alloy 10 per cent Cu, 1.2 per cent Fe, 0.2 per cent Mg, balance Al.

periods of time at a temperature estimated to bring about measurable relief of residual stress by plastic flow. It was not found possible to determine the magnitude of the residual stress in the as-quenched condition, for the reason that in several attempts the cylinder failed during the first boring operation. It may, however, be deduced

in three directions of one of the quenched and reheated cylinders. The maximum stress is in the longitudinal direction, with relatively lower stresses in tangential and radial directions. The curve of Fig. 3 gives the effect of time at a temperature of 225°C . (435°F .) on the maximum tangential stress in this series of cylinders. The residual

stress drops from a value that might have been near the tensile strength of the material (47,500 lb. per sq. in.) to a value in the neighborhood of 15,000 lb. per sq. in. in less than one hour at temperature. Thereafter the relief of stress at this temperature proceeds at a gradually decreasing rate.

A similar experiment was performed with the 52S alloy (2.5 per cent Mg, 0.25 Cr, balance Al) tubing in the hard-drawn condition. The tubing was $3\frac{3}{4}$ in. outside diameter by $2\frac{3}{4}$ in. inside diameter. Being in the hard-drawn temper, these tubes would be expected to have relatively high residual stresses remaining from the fabricating operations. Typical mechanical properties of 52S-H are: yield strength, 36,000 lb. per sq. in.; tensile strength, 41,000 lb. per sq. in.; elongation, 7 per cent.

The Sachs method for estimating residual stresses assumes a length of specimen at least three times the diameter. Table 1 gives the measurements involved in an analysis of a specimen of this tubing $11\frac{1}{4}$ in. long. In Fig. 4 the distribution of longitudinal, tangential, and radial stresses throughout the wall of the tubing is depicted graphically. As might be expected, contrary to the distribution in quenched sections, tension stresses are present in the surface of the tube with compression stresses at the inside wall. This distribution of residual stress is usual in tubing reduced primarily by drawing. Quite different distributions of stress are, however, set up by different fabricating operations. This is illustrated in Fig. 5, which gives the distribution of stress in a similar tube in which a relatively large portion of the reduction was effected by sinking rather than by drawing over a mandrel.

The machining and measurement of such lengths of tubing as are required by adherence to the ratio of 3:1 for length to diameter involved numerous mechanical difficulties as well as distinctly limited the number of specimens that might be obtained from the same individual tube. The

effect of a wide variation in the length of the specimen is illustrated by Fig. 6, which gives the distribution of stress in a specimen from the same tube as was utilized in the preceding experiment on drawn tubing. In this instance, however, a length of $3\frac{3}{4}$

TABLE 1.—*Dimensional Variations Obtained after Removal of Successive Layers from Interior of Drawn Tubing of 52S-H Alloy*

3.75-INCH OUTSIDE DIAMETER, 0.5-INCH WALL,
11.25 INCH LONG

Inside Diameter of Cylinder, In.	Length, In.	Length Change, In.	Diameter, In.	Diameter Change, In.
2.750	11.25936		3.7496	
2.875	11.25806	-0.0013	3.74932	-0.00026
3.000	11.25662	-0.00134	3.74916	-0.00026
3.125	11.25519	-0.00153	3.74890	-0.00026
3.250	11.25418	-0.00101	3.74891	-0.00039
3.375	11.25196	-0.00222	3.74816	-0.00045
3.500	11.25093	-0.00102	3.74765	-0.00045

STRESSES IN VARIOUS LAYERS

Diameter of Cylinder, In.	Longitudinal Stress, Lb. per Sq. In.	Tangential Stress, Lb. per Sq. In.	Radial Stress, Lb. per Sq. In.
2.750	-14,950 ^a	-11,950	0
2.875	-11,700	-9,000	-500
3.000	-8,350	-6,000	-740
3.125	-4,800	-3,000	-875
3.250	-1,100	0	-920
3.375	+2,650	+3,000	-825
3.500	+6,600	+6,000	-635
Outside layer...	+14,950	+11,950	

^a The negative or positive sign denotes, respectively, a compression or tension stress.

in. rather than $11\frac{1}{4}$ in. was used. The stress distribution with the shorter specimen is not particularly different from that determined on the long specimen. However, the magnitude of the maximum stress in all three directions is somewhat higher with the shorter specimen. Since the absolute value of the maximum residual stress was not important in the following experiment, and since it was far more important that all the specimens be obtained from the same length of tubing, a specimen length of 6 in. was used.

In addition to a specimen analyzed in the as-drawn condition, four other similar specimens were heated, respectively, 15 min., 30 min., 5½ hr., and 50 hr. at 150°C.

to that obtained on reheating quenched, cast 122-alloy cylinders, as shown in Fig. 3. Here again the residual stress initially dropped rapidly with time at the heating

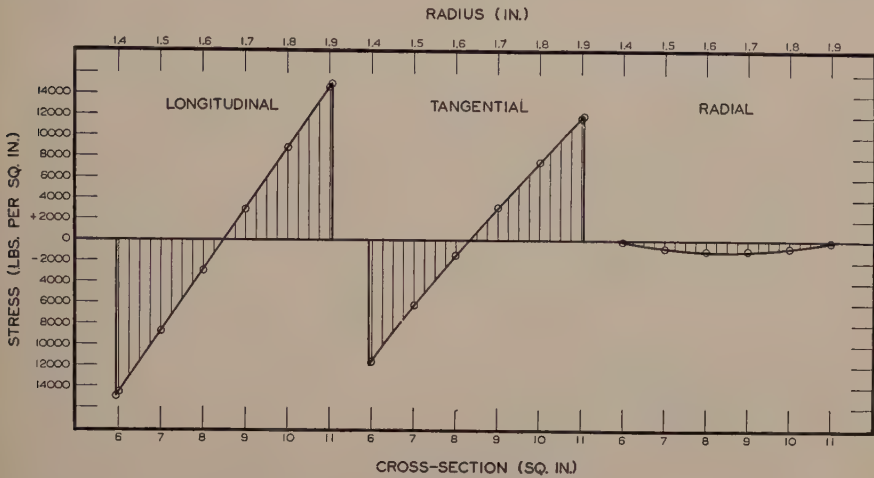


FIG. 4.—DISTRIBUTION OF RESIDUAL STRESSES IN 52S-H TUBING.

Alloy 2.5 per cent Mg, 0.25 per cent Cr, balance Al. 2.75 in. inside diameter, 3.75 in. outside diameter, 11.25 in. long.

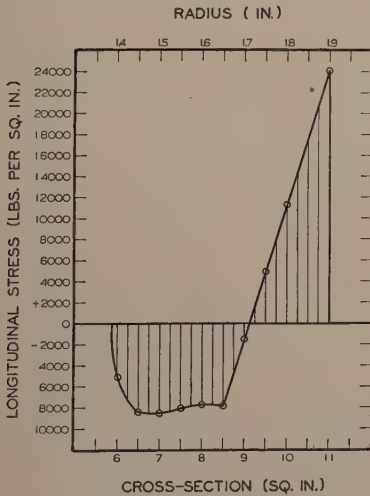


FIG. 5.—DISTRIBUTION OF RESIDUAL STRESS IN 52S-H SUNK TUBING.

Alloy 2.5 per cent Mg, 0.25 per cent Cr, balance Al. 2.75 in. inside diameter, 3.75 in. outside diameter, 11.25 in. long.

(300°F.). The maximum longitudinal stress in each of these specimens of tubing is plotted in Fig. 7 against the time at 150°C. (300°F.). This curve is very similar in shape

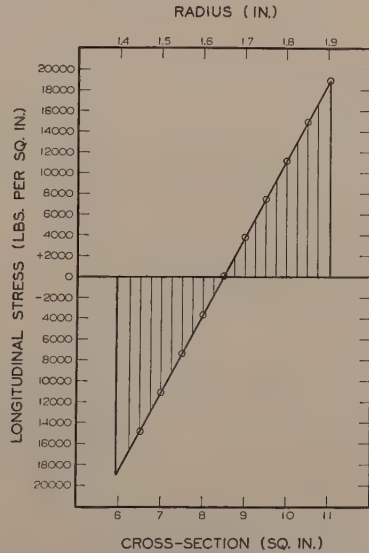


FIG. 6.—DISTRIBUTION OF RESIDUAL STRESS IN 52S-H DRAWN TUBING.

Alloy 2.5 per cent Mg, 0.25 per cent Cr, balance Al. 2.75 in. inside diameter, 3.75 in. outside diameter, 3.75 in. long.

temperature and then the relief of stress proceeded at a decreasing rate.

ESTIMATION OF RESIDUAL STRESS BY SLITTING METHOD

It is essential that the rate of relief of residual stress be known fairly accurately

this was plainly evident from the Sachs analysis. This apparent lack of sensitivity of the Crampton method may be the result of a redistribution of stress on reheating.

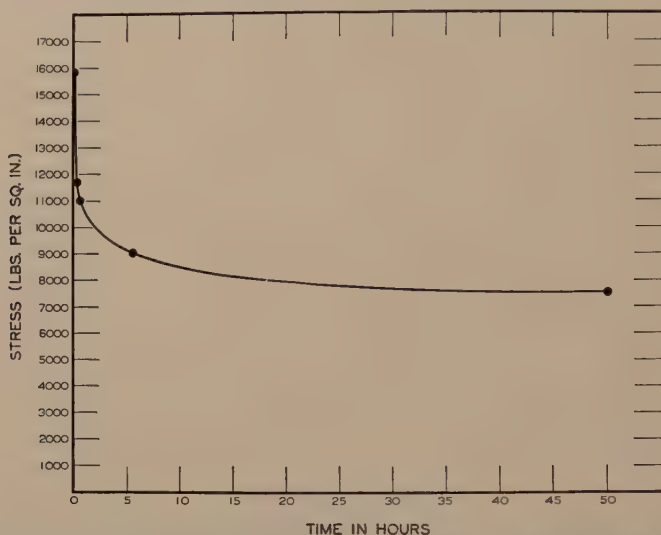


FIG. 7.—RELIEF OF LONGITUDINAL RESIDUAL STRESS AT 150°C. (300°F.) IN 52S-H DRAWN TUBING. Alloy 2.5 per cent Mg, 0.25 per cent Cr, balance Al. 2.75 in. inside diameter, 3.75 in. outside diameter, 6.0 in. long.

over a considerable temperature range if the optimum combinations of properties are to be obtained, especially in precipitation-hardenable aluminum alloys. Obviously, the Sachs method of analysis cannot be used for obtaining expeditiously large volumes of data on a number of different alloys over a considerable range of temperature and stress conditions.

Some consideration was given to other methods of estimating residual stress, and in some instances comparisons were made between the various methods available. The slit-tube method as utilized by Crampton³ was compared with the Sachs method on the same material. The order of magnitude of the stresses revealed by the Crampton method was uniformly lower than that indicated by the Sachs analysis. Also, in certain temperature ranges of reheating, the Crampton method gave no indication of a reduction in residual stress, although

which is not evident in an analysis involving a determination of stress in one direction only. Similar experiments utilizing split-ring and tongue methods^{4,5} on thinner-walled tubes gave unsatisfactory results, especially when relatively low stresses were involved. The Dawidenkow⁶ method was not investigated, inasmuch as its application appeared not much simpler than the Sachs method. It was decided that these convenient methods were not applicable in this investigation, particularly since most of the products involved were not available in the form of tubing.

RELAXATION AND RELIEF OF RESIDUAL STRESS

It is obvious that the relief of residual stress involves the phenomenon of flow or creep. Creep characteristics, however, ordinarily are determined by measurement of rate of deformation at constant stress.

The relief of residual stress is concerned with flow under conditions of relatively constant deformation and decreasing stress. Flow under these conditions is sometimes referred to as relaxation. Relatively little investigational work has been done in this field. There are some indications of a quantitative relationship between relaxation and creep, but the data available at the present time are far too meager to permit the definition of any correlation. The important point for present purposes is the resemblance between the curves of Figs. 3 and 7 and the relaxation curves of Boyd⁷ and Davenport.⁸ This immediately suggests that an examination of relaxation characteristics might be a convenient means of estimating rates of relief of residual stress.

The quantitative determination of rates of relaxation is by no means simple, involving as it does the accurate measurement of a varying stress under conditions of relatively constant deformation; also, determinations must usually be made at elevated temperatures. For the purposes of this investigation, it was thought sufficient to determine at room temperature the variations in stress, with time at elevated temperature, of specimens maintained during the entire operation at a constant deformation. To achieve this end, a fixture was utilized which had been developed by Dr. William L. Fink during the course of a somewhat similar investigation. The fixture (Fig. 8) consists merely of a means for maintaining a small beam of rectangular cross section under constant deformation during reheating and measurement of the stress at room temperature.

Specimens $\frac{1}{16}$ by $\frac{1}{4}$ by 12 in. were machined from castings, sheet or tubing. They were given the desired heat-treatment and air-cooled to room temperature or quenched in boiling water. The width and thickness of the beams were measured accurately with micrometers.

In a typical procedure, a specimen is placed in the jig and the load applied by

lowering the movable rod in the center of the jig to the definite desired deformation of the beam. The adjustable rod is then locked in this position. The magnitude of

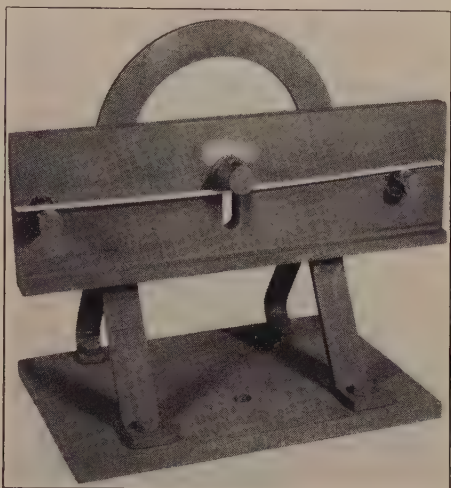


FIG. 8.—FIXTURE EMPLOYED FOR MAINTAINING A BEAM SPECIMEN UNDER CONSTANT DEFORMATION DURING REHEATING AND MEASUREMENT OF STRESS AT ROOM TEMPERATURE.

the load at the center of the specimen induced by the adjustable rod is measured by placing weights on a pan (suspended from the beam) until contact is just broken between the beam and the center of the rod. In order to determine accurately this separation point, an electrical circuit is set up between the specimen and the rod. This is accomplished by clipping one terminal of a battery to the vertical plate of the jig. This plate is in direct contact with the center rod, but is insulated from the two end rods by layers of mica. The other terminal of the battery is connected in series through a pair of headphones to one of the insulated end rod supports. When contact is broken between the aluminum specimen and the center rod, a distinct click is heard in the earphone. The weights on the pan are adjusted until the addition of a weight ($\frac{1}{2}$ or 1 gram) just breaks the beam-rod contact. The total suspended weight is then noted and, knowing the dimensions of the

beam and the distance between centers of the supports, the maximum fiber stress can be calculated from the simple beam formula.

center rod. The jig is heated until it reaches the desired temperature and then the beam is quickly inserted in the jig. When the beam has been heated the predetermined

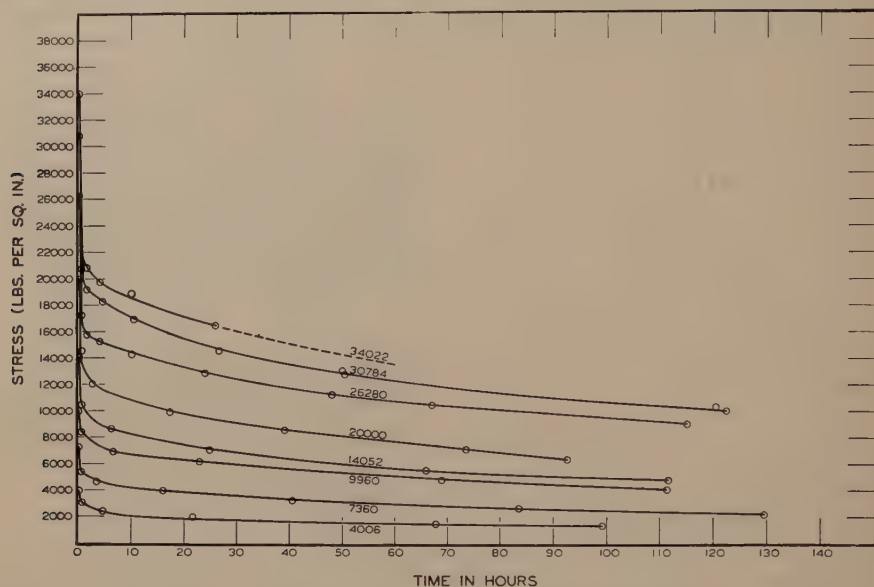


FIG. 9.—RELIEF OF STRESS IN BEAM SPECIMENS OF 122 ALLOY AT 225°C. (435°F.).

Alloy 10 per cent Cu, 1.2 per cent Fe, 0.2 per cent Mg, balance Al. Curves give stress-time relationships for different original loads. All specimens air-cooled from 500°C. (930°F.).

The specimen is removed from the jig and the jig is placed in an electric oven with mechanical convection, which has been

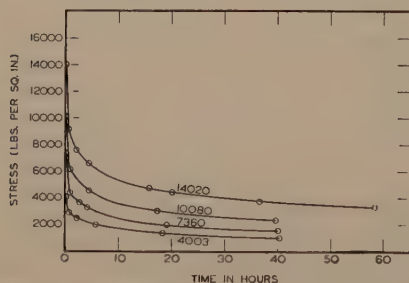


FIG. 10.—RELIEF OF STRESS IN BEAM SPECIMENS OF 122 ALLOY AT 250°C. (480°F.).

Alloy 10 per cent Cu, 1.2 per cent Fe, 0.2 per cent Mg, balance Al. Curves give stress-time relationships for different original loads; all specimens air-cooled from 500°C. (930°F.).

regulated for the temperature of the test. The thermometer is lowered through the well until it is in contact with the adjustable

length of time at the desired temperature, it is quickly removed from the fixture, which is then taken from the oven. A fan or air blast is used to facilitate cooling of the hot jig, and when it has reached room temperature the beam is reinserted and the load is again measured. This process is repeated until the desired relaxation of stress has been achieved.

The curves of Figs. 9 and 10 illustrate for 122 alloy the type of data obtained by this experimental procedure. The general similarity between these curves and that of Fig. 3 determined on solid cylinders for the same alloy may be noted. Here again the initial reheating results in a reduction of about 25 to 50 per cent in the initial residual stress, while extended heating is necessary to bring about appreciable further reduction. In general, the higher the temperature of reheating, the greater the initial reduc-

tion in stress and the greater the rate of subsequent relief. Also, the higher the initial stress, the generally greater the initial relief and the higher the rate of relief on prolonged heating.

deforms under stress. This is illustrated in Figs. 13 and 14, showing the rate of relief of residual stress in various alloys in the same structural conditions and submitted to approximately the same conditions of

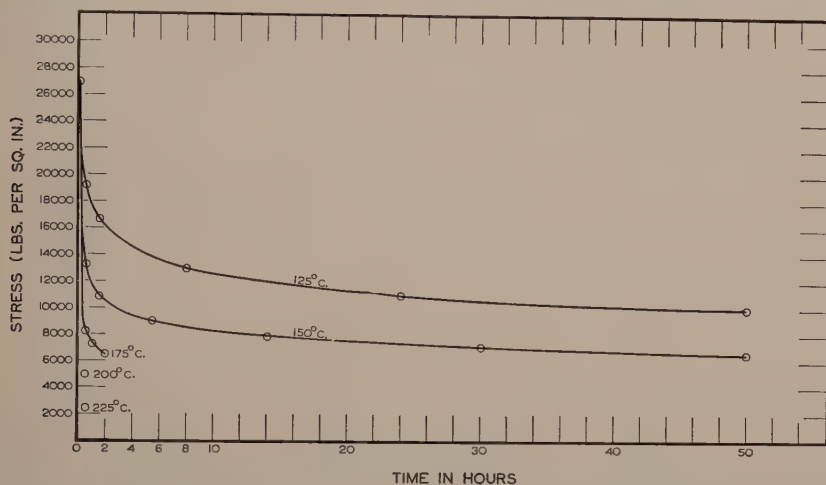


FIG. 11.—RELIEF OF STRESS IN 52S-H ALLOY BEAMS AT 125°, 150°, 175°, 200°, AND 225°C.

Alloy 2.5 per cent Mg, 0.25 per cent Cr, balance Al. Curves determined for original load of 26,850 lb. per sq. in. (75 per cent of yield strength of material).

Beam specimens of 52S alloy were prepared from 52S-H sheet, stressed to about 27,000 lb. per sq. in. and reheated to various temperatures. The results are plotted in Fig. 11, and here again the rate of relief of residual stress proceeds in a manner similar to that of the cast alloys. In Fig. 12 the curve for the rate of relief of residual stress in the hard-drawn 52S-H tubing determined by the Sachs method, together with the curve depicting the rate of relief of residual stress induced in the beam of hard-rolled sheet, are superimposed on the same diagram. The resemblance between the two curves is notable, and undoubtedly is a result of the essentially linear distribution of stress in the wall of the tubing and, of course, in the stressed beam. Apparently the method should have some utility in arriving at qualitative data upon which the selection of optimum heat-treatments may be based.

Naturally, the properties of an alloy determine the rate at which it plastically

stress and temperature. As is to be expected, the alloy showing the highest strength at the temperature of reheating relaxes at the slowest rate. This is, however, not always true, as is indicated in the curves of Fig. 15, giving the rates of relaxation for the same alloy in two different structural conditions. Here the beams heated 2 hr. at 540°C. (1000°F.) and quenched in boiling water show higher rates of relaxation, at least in some portions of the curve, than the same alloy heated 2 hr. at 500°C. (930°F.) and cooled in air. Beams treated according to the former procedure have an average yield strength of 10,900 lb. per sq. in., tensile strength of 25,750 lb. per sq. in., and elongation of 10.8 per cent in 2 in.; while air-quenching gives a yield strength of 9700 lb. per sq. in., a tensile strength of 24,750 lb. per sq. in., and an elongation of 12.0 per cent.

Reheating for the purpose of relief of residual stress usually brings about changes

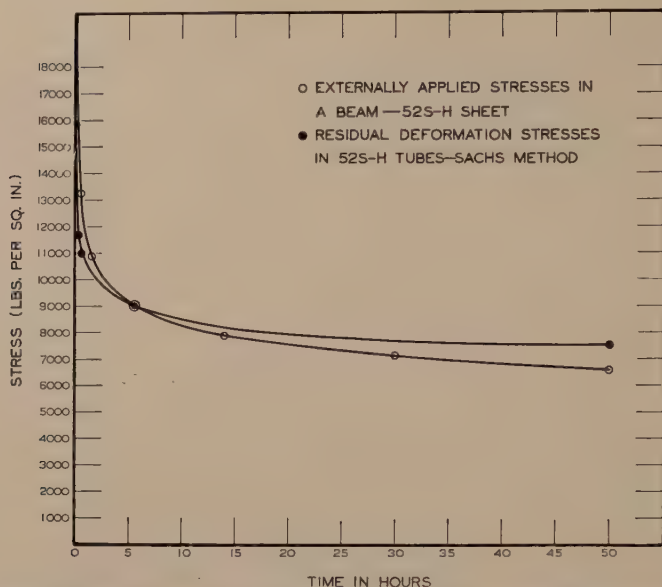


FIG. 12.—RELIEF OF STRESS AT 150°C. (300°F.) IN 52S-H DRAWN TUBING AND EXTERNALLY LOADED 52S-H BEAMS.

Alloy 2.5 per cent Mg, 0.25 per cent Cr, balance Al. Tubing 2.75 in. inside diameter, 3.75 in. outside diameter, 6.0 in. long. Beams 0.25 by 0.06 by 12.0 inches.

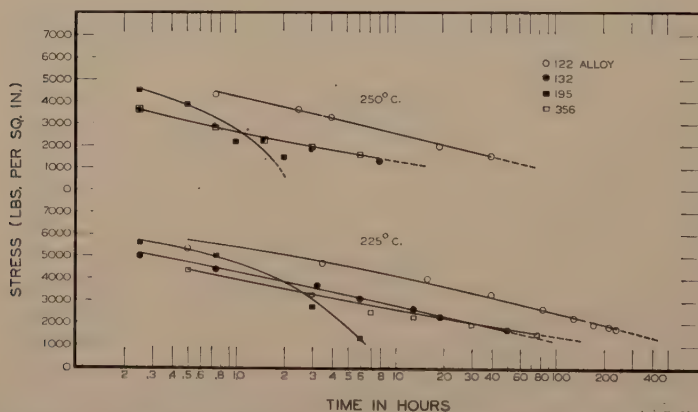


FIG. 13.—RELIEF OF STRESS IN ALCOA 122, A132, 195, and 356 ALLOY BEAMS AT 225° AND 250°C. (435° AND 480°F.).

Alcoa 122 alloy, 10 per cent Cu, 1.2 per cent Fe, 0.2 per cent Mg, balance Al.

A132 alloy, 0.8 per cent Cu, 0.8 per cent Fe, 12 per cent Si, 1.0 per cent Mg, 2.5 per cent Ni, balance Al.

195 alloy, 4 per cent Cu, balance Al.

356 alloy, 7 per cent Si, 0.3 per cent Mg, balance Al.

Curves determined for an original load of 7000 lb. per sq. in. All specimens air-cooled from 500°C. (930°F.).

in various properties of the alloy, particularly if the material is of the heat-treatable variety. The rate at which these various properties change with time at a given

In work-hardened alloys, considerable flow, relaxation, or relief of stress can occur at relatively low temperatures without greatly affecting the mechanical properties

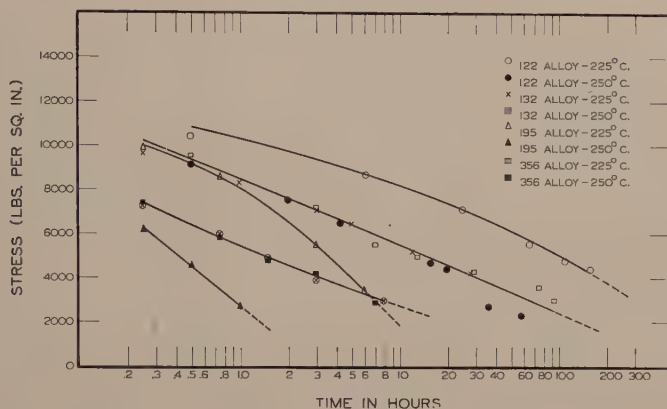


FIG. 14.—RELIEF OF STRESS IN SAME ALLOYS AS IN FIG. 13.

Curves determined for an original load of 14,000 lb. per sq. in. All specimens air-cooled from 500°C. (930°F.).

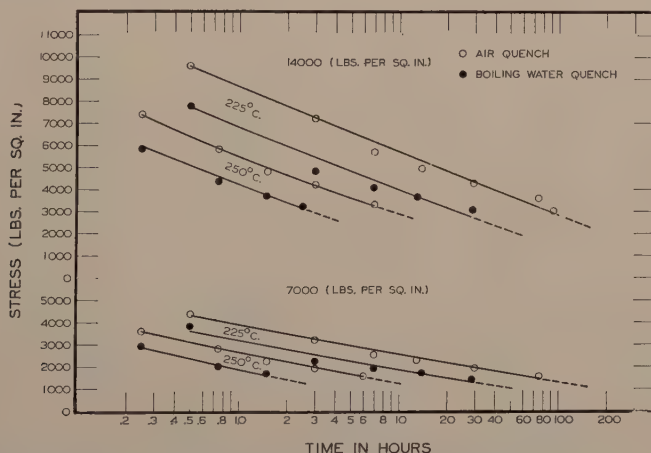


FIG. 15.—RELIEF OF STRESS IN AIR-QUENCHED AND BOILING-WATER-QUENCHED 356-ALLOY BEAMS AT 225° AND 250°C. (435° and 480°F.).

Alloy 7 per cent Si, 0.3 per cent Mg, balance Al. Curves determined for original loads of 7,000 and 14,000 lb. per sq. in.

temperature varies considerably. For example, the curves of Fig. 16 show the rate of relief of residual stress in 122 alloy at 225°C. (435°F.), the rate of precipitation-hardening at this temperature, together with the rate of change in density as determined by variations in lineal dimensions.

of the material. This is illustrated in Table 2, giving the properties of 52S-H after reheating for various periods of time at different temperatures. Of course this is one aspect of the general metallurgical phenomenon designated as recovery or change in some of the properties of a metal in the

direction of annealing, but without detectable recrystallization. X-ray diffraction analysis of the 52S-H sheet after the reheatings which markedly reduced the stresses, Fig. 11, Table 2, gave no evidence of recrystallization.

hardenable alloy quenched from a high-temperature solution treatment and the rate of decrease in residual quenching stress at the same temperature. The reheating temperature chosen, 225°C. (435°F.), is too high for the attainment of the maxi-

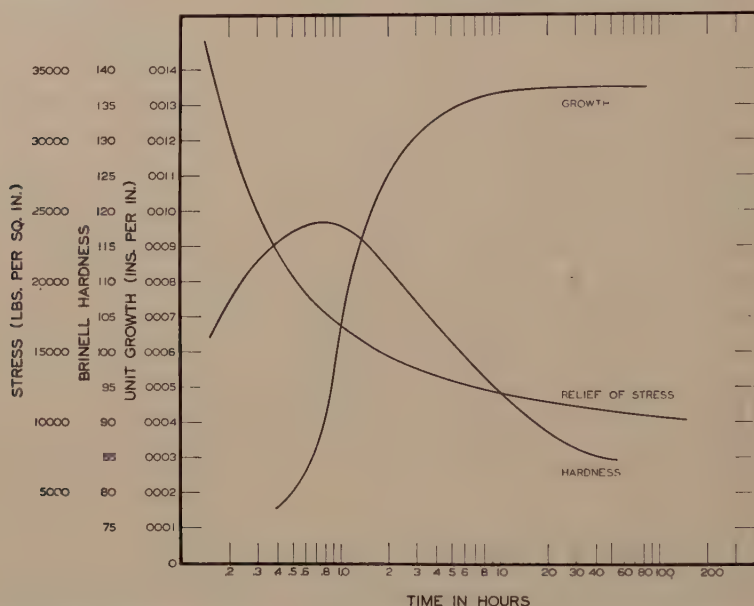


FIG. 16.—CURVES SHOWING RATE OF GROWTH, RATE OF RELIEF OF RESIDUAL STRESS, AND VARIATIONS IN BRINELL HARDNESS WITH TIME AT 225°C. (435°F.) IN ALCOA 122 ALLOY.
Alloy 10 per cent Cu, 1.2 per cent Fe, 0.2 per cent Mg, balance Al.

TABLE 2.—*Tensile Properties of 52S-H Alloy Sheet ($\frac{1}{8}$ Inch Thick) after Various Periods of Annealing*

Annealing Treatment	Yield Strength, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent in 2 In.
116 hr. at 125°C. (225°F.)	35,800	42,350	7.0
2 hr. at 175°C. (345°F.)	35,550	42,150	8.5
0.5 hr. at 200°C. (390°F.)	35,450	41,300	8.3
0.5 hr. at 225°C. (435°F.)	35,200	41,600	8.2
	34,450	40,225	8.5

PRACTICAL CONSIDERATIONS

The curves of Fig. 16 are important as indicating the relationship between the rate of hardening in a precipitation-

mium hardness and, thus, the tensile strength of which the alloy is capable of attaining at lower aging temperatures. Most heat-treatable aluminum alloys achieve maximum combinations of mechanical properties by precipitation at temperatures in the range 20°C. (68°F.) to 175°C. (345°F.). On the other hand, as indicated in the foregoing, 225°C. (435°F.) is too low a temperature to bring about complete relief, in reasonable periods of time, of the residual stresses induced by quenching. Heating at the optimum temperature for the development of maximum mechanical properties would, of course, result in even less relief of residual stress. The temperatures necessary for reducing the residual stresses to less than 1000 or 2000 lb. per sq. in. in reason-

able periods of time, say less than 10 or 15 hr., would result in decidedly inferior mechanical properties because of the rapid overaging occurring at such a temperature.

Fortunately, the mechanical properties that most heat-treatable aluminum alloys are capable of developing are not particularly affected by quenching rate within quite a wide range, and quenching stresses may be largely avoided by utilization of cooling rates just sufficiently rapid to give the desired mechanical properties. Some aluminum alloys, however, particularly those of the duralumin type that are not aged at elevated temperatures, develop maximum resistance to corrosion only when drastically quenched from high-temperature solution treatments, although slower rates of cooling may give approximately maximum mechanical properties. The attainment of maximum resistance to corrosion even in the duralumin-type alloys is usually necessary only where very thin sections are concerned. In such sections macroscopic residual stresses are usually low and not as troublesome as in heavy sections, the order of magnitude of quenching stresses increasing rapidly with section thickness. Also, the very highest order of resistance to corrosion is not as necessary in thick sections as in thin ones.

Fortunately, some alloys develop maximum resistance to corrosion with relatively slow cooling rates. This is true of heavy sections of the composition known as "Superduralumin" (14S) in which high mechanical properties are achieved by aging at elevated temperatures.

It has been found, as might be expected, that the residual quenching stresses in aluminum alloys are higher the greater the strength of the alloy, particularly at elevated temperatures. Even, however, with materials that develop the highest tensile strengths at room or elevated temperatures, the slowest cooling rate that will produce approximately maximum tensile properties results in residual stresses not

higher than about 5000 lb. per sq. in. This is true even in heavy sections of Y alloy, which has about the highest properties at elevated temperatures of any commercial alloy. Although quenching stresses of about 5000 lb. per sq. in. have never been found to cause difficulties in service, they may, however, cause distortion during machining of large complicated shapes such as crankcase castings for liquid-cooled aircraft engines. In such cases precipitation-hardening and stress relief may be combined by heating to temperatures somewhat higher and for shorter periods of time than are usually used for precipitation-hardening alone. For example, the normal precipitation-hardening treatment of an alloy such as might be used for an aircraft-engine crankcase might call for heating 1 to 5 hr. at 150°C. (300°F.). This reheating might not sufficiently reduce the residual quenching stresses. In such a case it was found that reheating for 2 hr. at 260°C. (500°F.) resulted in approximately the same tensile strength and hardness as obtained from a longer time at the lower temperature and with practically an elimination of the residual stress. It should be noted that, generally speaking, the elongations obtained by such high-temperature aging are usually lower even at the same tensile strengths than are obtained with lower-temperature aging. It may be taken as a generality that, for the purposes of relief of residual stress or reducing density changes, short-time exposures to the highest possible temperature consistent with the development and maintenance of satisfactory mechanical properties are usually far more effective than very extended times at lower temperatures.

Sometimes parts made from cold-worked materials such as cold-rolled sheet must be straightened following fabrication. This can be done, in some applications, by clamping the part in a fixture that maintains the desired shape and then reheating to slightly elevated temperatures. The

procedure described in the foregoing may be utilized for determining the proper period of time and temperature of reheating. Conditions may be so chosen that no great reduction in properties of the work-hardened material occurs. For example, it was found that circular plates of 14-gauge 52S-H sheet might be straightened, after a light machining cut on one side caused distortion, by loading sufficiently to obtain flatness and then reheating 2 hr. at 175°C. (345°F.). As indicated in Table 2, such reheating results in relatively minor changes in properties.

It has long been recognized in the trade that spring-type pistons in internal-combustion engines undergo changes during the very early stages of operation, which bring about a slight increase in clearance. Subsequently the piston will appear to be mechanically stable over very long periods of operation. This is evidently another manifestation of the initial rapid reduction of high internal stress on reheating to slightly elevated temperatures. The stresses are induced by pressure between cylinder wall and piston and are highest where the pressure is maximum. The heating during initial operation results in relaxation, thus automatically producing a better fit between the individual piston and cylinder than could ever be achieved by machining. The "beam" method described in the foregoing has been used to compare the behavior of various alloy compositions under such conditions and has been found to agree with the results obtained in motor operation.

(relaxation method) was devised and utilized for obtaining a qualitative evaluation of the rate of relief of residual quenching and cold-working stresses in a number of aluminum alloys.

3. Reheating to just below the recrystallization range for the specific amount of plastic deformation involved is necessary for practically complete elimination of residual stress.

4. Important reductions in residual stress may be effected by heating at much lower temperatures, in the precipitation-hardening range for most aluminum alloys, and satisfactory combinations of mechanical properties and relative freedom from residual stress are obtainable by judicious selection of reheating conditions.

5. For attaining low levels of residual stress by reheating, the temperature factor is more important than the time factor, short exposures to relatively elevated temperatures being much more effective than greatly extended exposure to lower temperatures.

6. When other considerations permit—as, for example, resistance to corrosion—the most satisfactory combinations of high mechanical properties and low levels of residual stress can be obtained in heat-treatable aluminum alloys by cooling from the solution temperature at the slowest rate consistent with the development of the desired mechanical properties. In most cases this rate will be sufficiently slow to prevent the formation of quenching stresses of a high order of magnitude.

SUMMARY AND CONCLUSIONS

1. Of a number of methods examined for following the relief of residual stresses in aluminum alloys on reheating to elevated temperatures, the Sachs method was judged to be the most reliable.

2. Using this method as a criterion, a simpler and more economical method

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DISCUSSION

(*William L. Fink presiding*)

P. W. BAKARIAN,* Midland, Mich.—Have the authors done any work on the relief of residual stresses by means of deformation? I bring up the subject because of the findings in a recent paper on the determination of residual stresses in an aluminum alloy of 17S composition, which shows residual stress determinations of the same order of magnitude reported in the present paper.⁹ However, it was further dis-

closed that small amounts of deformation completely eliminated and sometimes reversed the residual stresses in the metal.

I would like to hear the author's comments on this subject and its possible application in commercial practice.

L. W. KEMPF (author's reply).—We have not investigated the relief of residual stresses by means of plastic deformation. We are aware that plastic deformation brings about a redistribution and perhaps relief of residual stress under certain conditions, but we are not aware of any commercial application of this method of redistributing residual stresses resulting from rapid cooling from elevated temperatures.

* Dow Chemical Co.

⁹ A. Von Zeerlander: *Jnl. Inst. Metals* (1941) **67**, 87-99.

Preferred Orientation in Rolled Magnesium and Magnesium Alloys

By P. W. BAKARIAN,* STUDENT ASSOCIATE A.I.M.E.

(Philadelphia Meeting, October 1941)

PREVIOUS determinations^{1,2,3} of the texture of magnesium and its alloys have shown only slight variations in the principal features of the structure. This investigation presents pole figures for magnesium and two of its alloys, in which differences of some magnitude will be shown.

Schmid and Wassermann have considered the texture of magnesium in analogy with that of zinc—also a hexagonal lattice. Whereas the zinc texture is said to be derived primarily through basal slip and secondarily through $\{102\}$ † twinning, the $\{102\}$ twinning is considered impossible at the later stages of the rolling in magnesium because of its smaller axial ratio. This state of affairs appears reasonable for pure magnesium, but for alloy textures the situation is more complex.

A double orientation similar to that found in zinc has been reported by J. D. Hanawalt,⁴ and the addition of small amounts of calcium to magnesium and its alloys to produce a double texture was noted by J. C. McDonald.⁵ The pole figures of this investigation, using an improved X-ray technique, show these various textures.

The dependence of directional properties of rolled sheet on modifications of texture is well recognized. Correlation of physical properties with existing texture should be even more significant if quantitative valuations are attached to the various areas on

the pole figures. Such a quantitative technique is developed herein.

EXPERIMENTAL METHOD

Two alloys were used, besides high-purity magnesium. In each case, the metal was extruded to bars $\frac{1}{2}$ in. thick and hot-rolled to a thickness of about 0.075 in. It had been established previously that such a reduction was more than sufficient to eliminate the extruded structure. The rolling proceeded in the same direction as that of the extrusion, without any cross rolling. The temperatures corresponded to normal commercial practice, averaging around 600°F.

A unique method of preparing the sample was developed in this work. Instead of using a flat specimen, a stem of the metal was cut out of the rolled sheet in the desired direction (rolling direction) as shown in Fig. 1. From a sheet of 0.075 to 0.065-in. gauge, the stem was cut to a square cross section with a jeweler's saw, rounded with a file and polishing paper to a diameter of 0.060 in. and evenly etched in dilute hydrochloric acid to a diameter of 0.038 ± 0.001 in. In this way, a cylinder of the original sheet with its axis in the desired direction was produced. By using this type of specimen for the pin-point pictures, any variance in the absorption of the diffracted beam at the various angular settings of the specimen, was completely eliminated.*

* Although in the general case a spherical specimen alone would give a completely equivalent absorption effect in all directions of X-ray beam diffraction, in the present work only cylindrical symmetry was required, because of the concentration of basal reflections in the positions symmetrical with respect to the specimen axis.

Manuscript received at the office of the Institute Dec. 2, 1940; revised March 6, 1941. Issued as T.P. 1355 in METALS TECHNOLOGY, August 1941.

* Dow Chemical Co., Midland, Mich.

† References are at the end of the paper.

† The notation of Edmunds¹² has been followed in this paper. The conventional dot for the missing index is omitted.

The X-ray apparatus consisted of a sealed G.E. tube with a molybdenum target. All the pin-point photograms were taken with conditions as equivalent as possible. The film was placed 6 cm. from the specimen and given a 35-min. exposure at 25 ma. and 42 kv. Constant developing procedure was maintained throughout. Generally 10 pictures were taken of each specimen at intervals of 10° rotation about the rolling direction. From these X-ray photograms, pole figures for the basal plane were plotted, using a Wever chart.^{6,7} In estimating the intensity of the reflections, a reproducible intensity scale of a series of intensity ratings was used. This scale was prepared⁸ by exposing an X-ray film to a monochromatic source, reflected from the cleavage face of a calcite crystal under conditions in which the film darkening was proportional to the change of exposure time. From this scale of 14 intensities, ranging from values of 1 to 250, only five or six ratings were used in this work (for example: 75, 50, 30, 15 and 2). It was easily possible to differentiate the six intensity segments, for two reasons: (1) absence of

absorption variation with specimen rotation; (2) use of a contact comparison method, wherein the intensity scale is placed over the film to be read, in contact

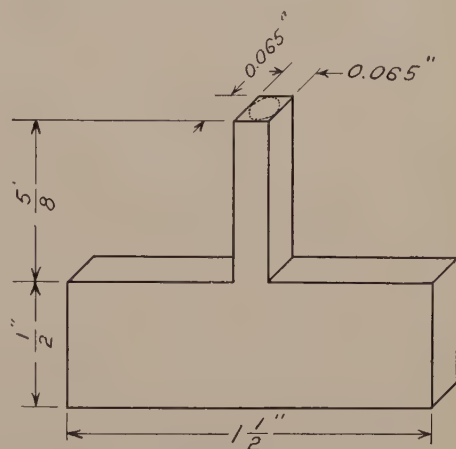


FIG. 1.—METHOD OF PREPARATION OF SPECIMEN.

with the ground-glass plate of a film illuminator. Since this intensity scale contains intervals of clear glass between adjacent intensity steps, movement of it over the diffraction rings aided in accurately determining the segments of differing intensity.

Since all diffraction photograms were given the same exposure and development treatment, the assigned intensity ratings are proportional, in heavily worked metal, to the relative amount of material reflecting at the various orientations; or, with a recrystallized structure, to the relative number of grains reflecting. This accurate proportionality was made possible through the development of the cylindrically symmetrical specimen.

In applying this linear relationship of intensity to orientation concentration, it is necessary to measure or calculate the actual spherical area represented by the different areas on the pole figure. A measure of this spherical area can be obtained by determining the number of solid angles contained in each of the pole-figure areas, by placing a polar stereographic net (divided radially

TABLE 1.—*Calculation of Orientation Percentages for Specimen No. 3^a*

Directional Section	Intensity Number	Area Solid Angle	Product Solid Angles and Intensity	Percentage of Material Oriented in Respective Areas
Rolling direction..	75	628	47,200	27.9
	50	545	27,200	16.2
	30	540	16,200	9.6
	15	410	6,150	3.6
	4	548	2,190	1.3
	<2	1376	2,760	1.6
Cross direction...			101,700	60.1
	75	10	750	0.45
	50	406	20,300	12.0
	30	1108	33,200	19.6
	15	510	7,660	4.54
	4	665	2,660	1.57
	<2	1352	2,700	1.60
			67,270	39.9

T.I.N. = 168,970.

^a Because of the symmetrical texture, it was necessary to make evaluations over only $\frac{1}{4}$ of the pole-figure basic circle.

and concentrically into 1° intervals) into coincidence with the pole-figure basic circle and counting the number of solid-angle units contained in each pole-figure area. The values of these counts multiplied by their respective intensity-rating numbers are representative of the amount of mate-

direction and cross direction (at the 45° radial line on the projection) were noted separately and the percentages were calculated accordingly. In this way a concept of the relative concentration of material oriented in the rolling direction and the cross direction may be obtained.

TABLE 2.—*Summary of Orientation Percentages in Rolling and Cross Directions for Specimens Investigated*

Specimen Number	Composition	Intensity Number	Percentage of Material Oriented		
			Rolling Direction Section, Per Cent	Cross Direction Section, Per Cent	Each Intensity Area, Per Cent
1	99.987 % Mg, 0.001 % Fe, 0.001 % Al, 0.001 % Si, and 0.010 % Pb.	250	34.2	15.5	49.7
		175	9.9	12.1	22.0
		150	8.3	5.7	14.0
		75	3.7	2.6	6.3
		40	2.4	2.4	4.8
		10	0.6	0.3	0.9
		≤ 2	1.0	1.3	2.3
			60.1	39.9	100.0
2	High-purity Mg (99.987 %) and 0.20 % Ca.	75	31.2	1.1	32.3
		50	14.6	31.4	46.0
		30	3.9	5.0	8.9
		15	1.7	4.7	6.4
		4	1.5	0.8	2.3
		≤ 2	2.1	2.1	4.2
			55.0	45.0	100.0
3	2.0 % Mn, 0.15 % Ca + Comm'l Mg (99.95 %)	75	27.9	0.5	28.4
		50	16.2	12.0	28.2
		30	9.6	19.6	29.2
		15	3.6	4.5	8.1
		4	1.3	1.6	2.9
		≤ 2	1.6	1.6	3.2
			60.1	39.9	100.0

rial oriented in the respective areas. The addition of all these products for each pole figure gives what is designated as the "total-intensity number." By taking the product of intensity number and solid-angle number for each area of a pole figure, and dividing by the "total-intensity number" of that pole figure, the percentage of the total amount of material found in the respective orientation areas of the pole figure is obtained. In order to get more definite information as to the amount of material present in the rolling direction or cross direction, the solid-angle count of the various areas of the pole figure above and below a line halfway between the rolling

The method of calculation for orientation percentages is illustrated in Table 1 with specimen No. 3. The rolling and cross-direction sections refer to the parts of the pole figure divided by the 45° lines and containing the respective directions. A summary of the orientation percentages for all three pole figures is presented in Table 2.

Throughout this investigation the pole figures have been derived for the basal plane (001) only. Although a basal-plane pole figure does not completely define the orientation unless accompanied by a pole figure of some other plane, for the rolled magnesium alloys studied here the crystals are found in all possible positions of rota-

tion about the basal plane normal as an axis.

RESULTS AND DISCUSSION

Fig. 2 shows the texture of high-purity magnesium (99.987 per cent Mg, 0.001 Al, 0.001 Si, 0.001 Fe and 0.010 Pb). As reported in previous investigations, the basal plane is largely concentrated parallel to the surface of the sheet. However, a marked spread is present around the cross direction, which extends to a position 53° from the sheet normal. The spread around the rolling direction is 28° . Approximately 97 per cent of the material in the rolled sheet is oriented in positions such that the c axis falls within an elliptical area with its major axis 100° in length along the rolling direction and minor axis of 50° along the cross direction. This increased spread in the rolling direction relative to cross direction is in part characteristic of the texture found by Schmid, Schiebold, and Caglioti and Sachs, but it was not as pronounced in their findings. On the pole figures of Caglioti and Sachs, and of Schiebold, an increased spread was discovered in positions intermediate between the rolling direction and the cross direction. This condition was absent in the present determination. The variations in texture may be caused by deviations in the purity of the magnesium. Schmid and also Caglioti and Sachs used magnesium of technical grade, while Schiebold, employing a magnesium-rich aluminum-zinc alloy, assumed that the same texture would be produced in the pure metal. Further evidence sustaining this conclusion is noted below, where pronounced alterations of the texture of pure magnesium are found with a small calcium addition.

The texture obtained when 0.20 per cent Ca is added to the high-purity magnesium (99.98 per cent) is illustrated in Fig. 3. The intense basal pole concentration is now located in elliptical areas whose centers are positioned 15° off the sheet normal, in the rolling direction. This split of the heavy

concentration area into separate sections is termed a double orientation. A more pronounced double orientation is derived in an alloy of 2.0 per cent Mn, 0.15 per cent Ca,

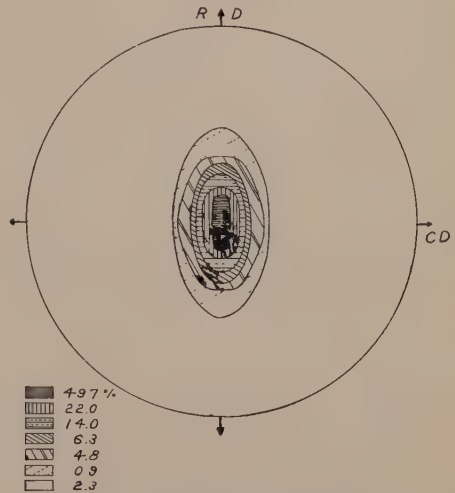


FIG. 2.—POLE FIGURE OF HIGH-PURITY MAGNESIUM, 99.987 per cent Mg, 0.001 Al, 0.001 Si, 0.001 Fe, 0.010 Pb.

and commercial magnesium (99.95 per cent) (Fig. 4). The position and extent of the most intense areas are in this case equivalent to the magnesium-calcium alloy, but a further decrease in concentration at the sheet normal position is caused by the splitting of the second intensity field.

The orientation percentage values of the two alloy specimens presented in Table 2 indicate that approximately 60 to 80 per cent of the material in each sheet is concentrated in the two most intense fields of the pole figure. Although the influence of these large concentration fields upon the directional physical properties may be well recognized, the importance of the less intense fields should by no means be minimized. For example, the direction and extent of spread existing in the third and fourth areas may greatly affect the directional yield-strength values. It is generally conceded that at room temperature translation in magnesium takes place along the

basal plane, especially during the initial stages of deformation.⁹ Grains with basal poles oriented 45° to the sheet normal will be in positions of high resolved shear stress

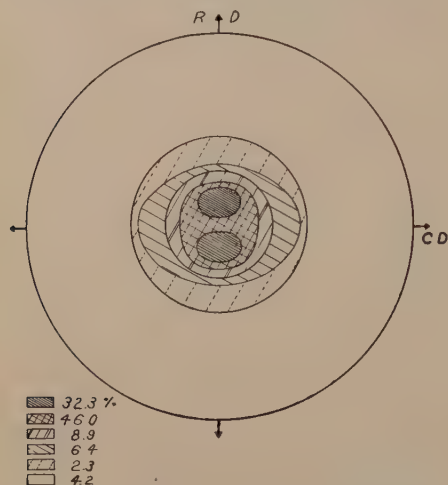


FIG. 3.—POLE FIGURE OF HIGH-PURITY (99.987 PER CENT) MAGNESIUM WITH 0.20 PER CENT CALCIUM.

along the slip plane. The yield strength depends on orientation concentration and the location of this concentration relative to the 45° position.

Considerations of the origin of the textures found in these alloys can be of only a speculative nature. Schmid's explanation of the texture of magnesium is founded on the mechanism of glide along the basal plane with consequent rotation of this plane into the surface of the sheet. This explanation appears acceptable if the rolling process is assumed to be a combination of compression and tension stressing. In zinc the double orientation is explained by twinning on the $\{102\}$ pyramidal planes. Translation along the basal plane is active in the initial stages of the deformation, moving the basal plane toward the sheet surface. In this position, the $\{102\}$ twinning would facilitate the deformation of the sheet, for it leads to extension in the rolling direction. After twinning, the basal plane in the twinned position is favorably oriented for further extension. This combination of twinning

and translation is thought to give rise to the double orientation in zinc. Twinning on the $\{102\}$ planes cannot take place in magnesium under similar conditions because it

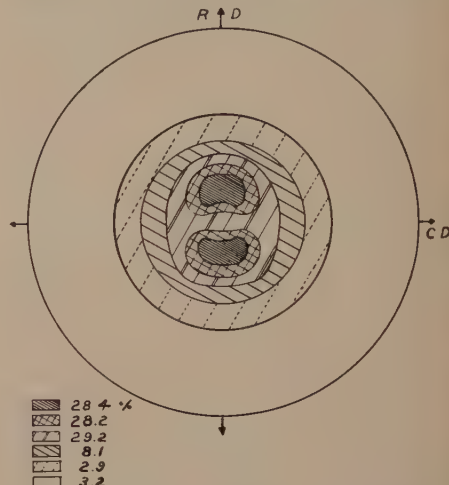


FIG. 4.—POLE FIGURE OF COMMERCIAL MAGNESIUM ALLOY WITH 2 PER CENT MANGANESE AND 0.15 PER CENT CALCIUM.

would lead to contraction of the sheet in the rolling direction.¹⁰ However, possibly an analogous explanation of the double orientation found in magnesium alloys may be drawn. Dr. J. C. McDonald, of this laboratory, has suggested that the twinning could be active on the $\{101\}$ planes instead of on the usual twinning plane, $\{102\}$. This is a possible explanation, for two reasons:

1. Twinning on the $\{101\}$ planes will result in extension in the rolling direction for magnesium alloys in much the same manner as $\{102\}$ twinning causes the extension in zinc.

2. $\{101\}$ twinning has been observed in the extension of single crystals of magnesium¹¹ at particular orientations. Moreover, it may be conceivable that a more general $\{101\}$ twinning sets in under the conditions of the stiffened lattice present in the alloyed metal.

Translation on a crystallographic plane other than the basal (001) plane may conceivably result in such a double texture also. In magnesium, translation on the

pyramidal planes has been observed during deformation at temperatures above 225°C.; similarly, alloying might likewise influence the choice of active glide planes.

SUMMARY OF RESULTS

1. An improved method for plotting pole figures having quantitative intensity fields is presented.

2. Pole figures for high-purity magnesium and two magnesium-rich alloys have been determined.

3. The significance of the intensity evaluations of pole figures in determining directional properties is discussed.

4. The existing textures are rationalized on the basis of single-crystal behavior.

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DISCUSSION

(P. T. Stroup presiding)

J. C. McDONALD,* Midland, Mich.—The author's excellent work in determining precisely the preferred orientations in magnesium and its alloys points the way to further studies whose purpose should be to discover the mechanism of deformation responsible for the splitting of the pole figure. Since the addition of Ca to Mg produces this effect, it would seem desirable to study the behavior of single crystals of that alloy.

By subjecting such crystals to deformations of various sorts, at several temperatures from the cold up through the hot-rolling range, it should be possible, through further X-ray work, to locate the planes of glide or twinning, which-

ever may be responsible for the effect. One thing seems certain; there must be a considerable change in the mechanism of deformation of the single crystal when Ca is alloyed with Mg.

As the author says, with what we know now, we can only speculate on the nature of this change. The hypothesis of {101} twinning seems most plausible, for the reasons cited. By studying the single crystal, it can be positively established whether this is the cause, or whether other factors are responsible.

G. EDMUNDS,* Palmerton, Pa.—I would be interested in having some further details as to the particular manipulation used to obtain the fine fiber specimens; 0.060-in. diameter by $\frac{5}{8}$ -in. length. These are stated to be prepared by sawing, filing, polishing and etching. The external distortion resulting from the mechanical operations involved is presumably removed by the etching, but it is rather a ticklish operation, I imagine, to prepare and hold a specimen so as not to get bending strains in the fiber.

Several years ago we tried to make a correlation between directional mechanical properties and preferred orientations in rolled zinc, such as Mr. Bakarian has talked of in a rather general way on magnesium. Our (qualitative) pole figures did not lead to a worth-while correlation with variations of tensile strength and elongation, electrical and thermal conductivity, thermal expansion, or other properties. I should like to know whether Mr. Bakarian has any detailed information showing such a connection.

Since Mr. Bakarian's paper was submitted to the Institute another paper¹³ on the subject of orientation in rolled magnesium alloys has been published. I had hoped to be able to make some comparison today, but did not have time to prepare a discussion.

P. W. BAKARIAN.—In answer to Mr. Gerald Edmunds' query for further details on the method of specimen preparation, I must admit that the manipulation is a "ticklish" one. But once the stem is cut to a square cross section, and this can be easily accomplished with a very fine jeweler's saw, it remains only to round off the four corners. To facilitate this, the stem was

* New Jersey Zinc Co.

¹³ D. E. Thomas: X-ray Examination of the Crystal Structures of Rolled Magnesium and a Magnesium Alloy. *Jnl. Inst. Metals* (1941) **67**, 173-176.

* The Dow Chemical Co.

cut to 1-in. length first, and the extra length used to clamp the specimen to the edge of a 1-in. steel plate. With one end thus clamped and the other held firm by hand, the corners were gently rounded over the $\frac{5}{8}$ -in. portion of the stem. This done, the extra length was sawed away and fine emery paper polishing carried out by rotation between the fingers.

The absence of strains of consequential

magnitude produced by the outlined manipulation was verified by the complete absence of distortion in the X-ray reflections from large-grained recrystallized material similarly treated.

Although correlation of properties with texture has been possible, the limited information so far obtained makes it necessary to await additional data before definite conclusions can be presented.

Corrosion Studies of Magnesium and Its Alloys

BY J. D. HANAWALT,* MEMBER A.I.M.E., C. E. NELSON* AND J. A. PELOUBET*

(Philadelphia Meeting, October 1941)

THE subject of the salt-water corrosion resistance of magnesium alloys is somewhat like that of the pitting of stainless steels, in that it involves a relatively small percentage of the applications but receives a much greater proportion of the publicity. Actually magnesium alloys are in use in many exterior applications as well as interior, with no trouble from corrosion. Magnesium and its alloys have a striking stability against atmospheric attack, being far superior to iron. Specimens exposed unprotected to atmospheric weathering for 10 years show only a superficial surface-film formation.

The basic nature of magnesium and of its important alloys is that they are also resistant to the attack of salt water even in an unprotected state, giving substantially no loss in weight after one year of alternate immersion in 3 per cent NaCl solution (Fig. 1). This basic behavior is often masked because of the extreme sensitivity of these alloys to certain impurities and combinations of impurities. It is known, and the subject of increasing emphasis, that higher purity leads generally to greater stability for many materials, non-metallic as well as metallic. However, a review of the literature on the corrosion factors in magnesium alloys shows that almost all researchers worked with base metal in which metallic impurities varied in uncontrolled amounts. The major factor, that of metallic impurities, probably

greatly overshadowed the effects of minor ones such as flux inclusions, nonmetallic impurities, porosity, metallographic state, which these researchers presumed to study.

In the present investigation the first observation of interest is that whereas magnesium of commercial purity (99.9 per cent pure) has a corrosion rate in alternate immersion in 3 per cent NaCl solution at room temperature of anywhere from 5 to 100 mg. per sq. cm. per day, the corrosion rate of high-purity magnesium is 0.15 ± 0.05 mg. per sq. cm. per day. The principle followed in the experiments was to add to such base magnesium other elements, singly and in combination, in controlled and known amounts and to observe the corrosion behavior of the resulting alloy.

These experiments show the existence of what may be called "tolerance limits" of magnesium and some of its alloys for certain impurities. The extremely small percentages of impurities involved and the sharpness of the corrosion discontinuities appear to be quite unpredictable.

In order to carry on this work, it was necessary to develop an analysis technique suitable to the problem. In some cases it was necessary quantitatively to analyze impurities to less than 0.001 per cent. The experimental data to be presented are based on observation of about 5000 alloy specimens and on more than 50,000 quantitative analyses.

While the primary purpose of this paper is to present the experimentally obtained data on corrosion rates as a function of composition, and particularly to demon-

Manuscript received at the office of the Institute Dec. 13, 1940; revised April 14, 1941. Issued as T.P. 1353 in METALS TECHNOLOGY, September 1941.
*The Dow Chemical Company, Midland, Michigan.

strate the existence of sharp tolerance limits for certain impurities, it would

generally accepted theories of corrosion behavior of metals. To this end, preliminary results are included from experiments on spot spectrographic analysis and metallography, on solution potential and over-voltage measurements, and also on electron diffraction studies of the all-important film formations.

The great majority of the alloy compositions studied have been made on 100-gram melts, which are just large enough for analysis and corrosion samples. In a later section of this paper, however, are reported results on material made in full production-scale melts and fabricated into standard test bars, from which the effect on mechanical properties of exposure to salt solution has been obtained.

CORROSION AS A FUNCTION OF ALLOY COMPOSITION

EXPERIMENTAL METHODS

Magnesium Purification Technique

Metallic magnesium as available commercially has the following typical analysis

	PER CENT		PER CENT
Fe.....	0.030	Al.....	0.01
Ni.....	<0.0005	Mn.....	0.002
Cu.....	<0.005	Pb.....	<0.001
Si.....	0.004	Na.....	<0.005

and is therefore unsuitable for the study of corrosion behavior of magnesium because of the presence of several elements in amount sufficient greatly to influence the corrosion rate. High-purity magnesium was produced by a special vaporization technique, since it was found that magnesium nonuniform in iron content was obtained by simple vaporization. Good purity magnesium could be produced at a satisfactory rate by distilling the metal from a magnesium-lead alloy and passing the vapors through a filter. After purification the magnesium is stripped from the condenser and representative samples are taken for routine analyses and control corrosion tests. Crystals of this purified

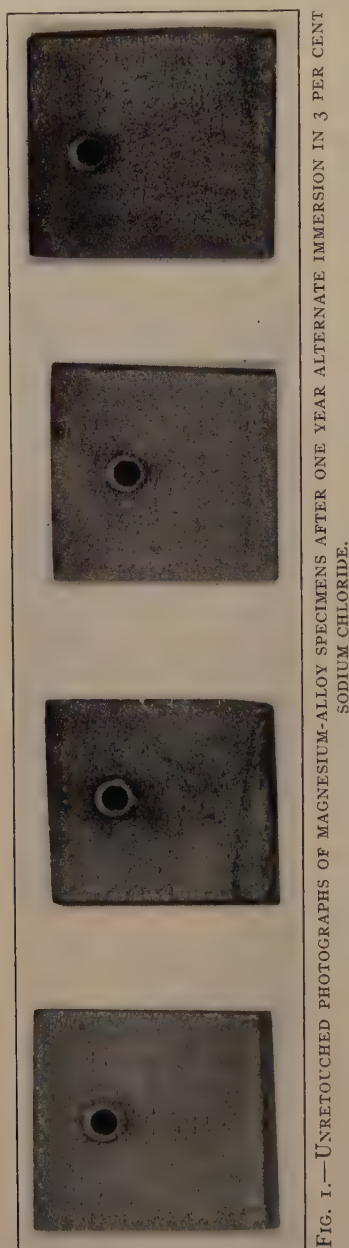


FIG. 1.—UNRETOUCHED PHOTOGRAPHS OF MAGNESIUM-ALLOY SPECIMENS AFTER ONE YEAR ALTERNATE IMMERSION IN 3 PER CENT SODIUM CHLORIDE.

naturally be of interest to ascertain whether the results can be explained in terms of any

magnesium are only superficially corroded even after exposure of a year or more to 3 per cent NaCl solution. The original technical magnesium would be entirely corroded away in several days if exposed to 3 per cent NaCl solution. A typical analysis of the purified magnesium product follows:

	PER CENT		PER CENT
Fe.....	<0.001	Na.....	0.002
Ni.....	<0.0001	Mn.....	<0.0005
Al.....	<0.001	Pb.....	<0.01
Ca.....	<0.001	Si.....	<0.001
Cu.....	<0.0001		

Pure Alloy Production Technique

The melting and alloying of the superpurity magnesium also required the development of a special technique and a careful selection of alloying materials, so that the desired compositions could be made without contamination by other undesirable elements.

It was discovered that superpurity magnesium could not be melted in an iron or steel crucible and the molten metal could not be contacted with tongs or other apparatus made of these materials because of the tendency of the alloy to pick up iron. Recourse was necessary, therefore, to materials of a refractory type, of which solid graphite, plumbago, carbon-lined silicon carbide (Tercod) and sillimanite were most satisfactory. The great bulk of the alloys for the present experiments were made in sillimanite or plumbago and spectroscopically pure graphite was used for stirring rods, sampling devices and thermocouple wells. Magnesium may not be melted in the plumbago or sillimanite crucibles without the use of a flux because the metal will attack the crucible and contamination of the melt with aluminum, iron and silicon will result. The use of the common magnesium melting fluxes, however, largely prevents this attack and at the same time protects the alloy from oxidation. Specially purified flux was used in the amount of 10 to 30 per cent of the weight of the metal. The bulk of the flux was

melted in the crucible and when hot the slightly preheated pieces of the weighed magnesium and necessary alloying constituents were added to the crucible with a careful sprinkling of powdered flux to inhibit burning. When the entire charge was in and thoroughly molten, the alloy was stirred carefully with a graphite rod several times at intervals of a few minutes. Quiet standing for 5 to 15 min. was then allowed, and finally the crucible was removed from the furnace, after which the charge froze and was then cracked out of the crucible, and the frozen flux washed from the metal. This simple technique avoided pouring of the metal and the consequent difficulties due to very small batches and danger of contamination. The finished alloys were then cut into samples for analysis and corrosion, as will be discussed later.

It has been stated in the literature that such substances as MgO, Mg_3N_2 , magnesium oxychloride or chlorine are appreciable factors in the corrosion of magnesium and its alloys. In order to check the present experimental procedure, and because of the possibility of the occurrence of these compounds in the production or fabrication of magnesium, it was considered advisable to investigate the behavior of such substances. It was found, providing harmful metallic impurities were not simultaneously introduced, that the following materials have no significant effect on the corrosion of high-purity magnesium and its alloys: CaC_2 , NH_4Cl , NH_4BF_4 , S, Mg_3N_2 , MgO, $MgOCl_2$, C, He, N_2 , CS_2 , C_2H_2 , CO, CO_2 , H_2 , H_2S , HCl, Cl_2 , CH_4 , SO_2 , O_2 , natural gas and air. It was also found that flux inclusions did not accelerate the corrosion rate of superpure alloys in 3 per cent NaCl solution.

The process and equipment for making the pure alloys having now been briefly outlined, some further consideration will be given to the selection and preparation of the alloying materials used.

Aluminum.—Commercial aluminum contains far too much iron, nickel and silicon for use in these experiments, so a special grade of aluminum, which contained only about 0.005 per cent iron and other impurities in very small amounts, was used.

Zinc.—Fortunately, in this case the regular commercial grade of Horsehead zinc is of satisfactory purity.

Manganese.—Commercial metallic manganese or hardener alloys of aluminum and manganese have until very recently contained far too much iron and nickel to be of use in the production of pure alloys. It had, however, been previously known that manganese can be added to magnesium alloys by the reduction of MnCl_2 ,¹ and since the latter salt is available in a very pure state this affords a good source of pure manganese. For the most part, hardeners of pure magnesium with 2.0 per cent manganese were made in large batches, and then parts of this pre-alloy were added in the correct proportions to smaller melts as required.

Iron.—Normally iron was added to the pure alloys, when desired, through the use of a pre-alloy made by reducing pure FeCl_3 with pure magnesium or a pure magnesium-base alloy. It was necessary to mix the FeCl_3 to be reduced with a proportion of the regular melting flux before adding it to the molten alloy, in order to prevent the loss of the FeCl_3 by excessive vaporization. Iron contents of 0.03 per cent or slightly over may be obtained in the binary magnesium-iron alloy by the foregoing technique. Iron can be added by direct contact with molten magnesium at elevated temperatures, but such a procedure is not dependable for uniform or predictable compositions.

Nickel, Copper and Lead.—Since nickel, copper and lead are available in a high degree of purity, and alloy readily with magnesium, they may be added directly to the magnesium alloy. Owing to the

extremely small amount required and the fine control of uniformity and quantity desired, the general practice was to make pure pre-alloys of magnesium or magnesium-base containing 0.01 or 1.0 per cent of the metals and then add aliquot portions of these to the intermediate alloys.

Silicon.—Silicon was perhaps the most troublesome of all the elements to add because of the lack of a source of high-purity silicon and the consequent tendency to introduce simultaneously into the alloy excessive amounts of other impurities. After many more or less successful attempts to reduce various pure silicon compounds, it was finally found that the best technique was to form a pre-alloy by using commercial 97 per cent silicon (ferrosilicon or 80 per cent aluminum, 20 per cent silicon hardeners), adding these to very pure magnesium or magnesium alloys in a proportion sufficient to produce a final silicon content of 1.0 to 10.0 per cent, and then removing any iron thus added by a precipitation treatment, so that the end product would be a pure magnesium-base alloy containing appreciable silicon but very little iron. This pre-alloy could then be analyzed and used in making other silicon-containing alloys.

More Complicated Alloy Additions.—The use of hardeners or pre-alloys, as has been previously mentioned, made the production of the more complicated combinations of elements possible. In practice, large batches of the various classes of pure base alloys were made up with no impurity additions and also with individual and varying amounts of the different elements to be studied. In this way, through the use of some 50 to 100 base alloys, almost any desired alloy could be made by mixing the proper group of base alloys in calculated proportions, without fear of altering the general alloy compositions by such mixing.

Methods of Analysis (See Appendix A)

Most of the analyses were made by a spectrochemical method. Occasional check

¹ References are at the end of the paper.

determinations were made by dependable chemical procedures.

In order to compare the composition of small corroded areas on a particular specimen with the composition of the non-corroded areas, it was necessary to use a procedure somewhat different from that described in Appendix A.

Samples of the areas to be studied, weighing 10 to 20 mg. each, were taken by use of a small drill, the diameter of which was less than the diameter of the area to be sampled. This material was dissolved in dilute sulphuric acid and the solutions were brought to a concentration of 5 per cent based on the magnesium. On each one of a pair of spectroscopically pure graphite supporting electrodes, 0.03 ml. of this solution was placed and then dried. The resulting salt was excited by means of a 2200-volt a.c. arc. From this point on the analytical procedure was identical to that described in Appendix A.

Specimens selected for this type of analysis were treated in several different ways prior to sampling. The first group of specimens was subjected to the regular corrosion test and then samples were taken from the corroded and noncorroded areas. Many of the corroded areas showed an iron content as high as 0.05 per cent while the noncorroded areas contained less than 0.002 per cent. However, there were cases where there was no difference in the iron content of the two areas after corrosion. Later tests indicated that the reason for this probably was that most of the iron had already left the corroded area either by dissolving in the corroding medium or by being mechanically removed as the magnesium around the iron particles dissolved.

The next group of specimens was subjected to the corroding medium only until the bad areas began to appear. All samples taken from these specimens showed greater iron concentrations in the corroded areas. Eleven different specimens analyzed in this manner showed iron concentrations in the

corroded areas varying from 5 to 50 times greater than the iron concentration of the noncorroded areas of the same specimen. A specimen treated in this same manner was analyzed by microchemical methods using the $\alpha\alpha'$ dipyridyl reagent. This analysis showed 0.0015 per cent iron in the good areas and 0.015 per cent iron in the corroded or bad areas.

A third series of samples was taken in the following manner. A specimen was cleaned and polished on one surface. This surface was carefully mapped and approximately 100 samples were taken from areas over the entire surface. The specimen was then immersed in the corroding medium until corrosion spots appeared. The small samples previously taken were then divided into two groups, one group being taken from the areas that corroded when placed in the corroding medium and the other group from areas that did not show attack. The iron content of the first group of samples was 0.008 per cent. The iron content of the second group was 0.0014 per cent.

In a fourth method a specimen was mounted under the microscope and a drop of 3 per cent NaCl solution was placed on it. The action of this solution was observed just long enough to locate definitely the source of attack, indicated by the evolution of bubbles of hydrogen. This area was then marked and washed with distilled water. The sample taken at this area contained 0.05 per cent iron. The iron content of a sample taken from the unattacked area contained 0.001 per cent iron.

In addition to analysis for iron, all of the above-mentioned samples were analyzed for nickel and chromium, two other metals that could cause increased corrosion. In no case was nickel or chromium detectable by either the spectrochemical or microchemical techniques.

Corrosion Testing

The specimens produced by the alloying technique described were subjected to a

standardized corrosion testing procedure. At the same time an accurate spectroscopic analysis of the impurity content was obtained. The actual specimens for corrosion testing and analysis were carefully cut from sections of the alloy that were known to be uniform and free from inclusions of flux. The corrosion sample was cut to a uniform size of $\frac{1}{4}$ by 1 by $1\frac{1}{2}$ in. along with the two analysis electrodes $\frac{1}{8}$ by $\frac{1}{2}$ by $\frac{5}{8}$ in. each.

For testing purposes, the specimens were first drilled near one end to accommodate a $\frac{1}{8}$ -in. glass hook. Subsequently the samples were ground all over on a clean No. 50 grit rotating abrasive cloth. This abrasive was of an aluminum oxide type, which did not harmfully contaminate the metal being ground. Finer finishes were of no additional value. The grinding was carried deep enough to eliminate all saw marks and original surfaces. Careful handling permitted the omission of a degreasing operation before the corrosion test.

Before the corrosion test, the samples were weighed to the nearest milligram and measured to the nearest millimeter. From the latter figures the original areas were calculated.

The standard corrosion test is essentially an alternate immersion-emersion in 3 per cent NaCl solution. The cycle consists of $\frac{1}{2}$ min. in the solution followed by 2 min. in air. During the latter time interval the specimens do not completely dry.

The specimens were dipped into individual glass containers as a means of avoiding the contamination of one specimen with corrosion product from another. At frequent intervals, distilled water was added to the containers to make up for loss by evaporation. This not only provides a more uniform concentration of NaCl but ensures a complete wetting of the samples on each cycle. Every two or three weeks (or oftener if necessary) the test solutions were renewed in order to prevent undue accumulation of corrosion product.

The temperature of the air and salt solution was that of the surrounding room, and was within the range of 60° to 100°F. It should be pointed out here that impure specimens corrode more rapidly than pure alloys with increase in temperature, while the corrosion rate of the latter is independent of the room-temperature changes. Thus, while working with specimens of low corrosion rate in determining impurity tolerance limits, the normal temperature variation is not an essential factor.

The corrosion test was continued for a period of 16 weeks. Specimens that did not survive the entire time were noted as destroyed. At the end of the test period, the samples were prepared for the final weighing by a complete removal of all corrosion products. This was accomplished by means of a 1-min. immersion in boiling 20 per cent CrO_3 solution to which has been added 1 per cent AgNO_3 .³ A CrO_3 solution alone does not appreciably attack magnesium or its alloys, but a considerable amount of sodium chloride is carried over to the cleaning bath within the corrosion product. If this were allowed to remain in the cleaning solution, the resultant hydrochloric acid would attack the specimens and produce erroneous weight losses. Therefore, a concentrated AgNO_3 solution is added to the 20 per cent CrO_3 , yielding a fine precipitate of Ag_2CrO_4 . This Ag_2CrO_4 reacts in turn to precipitate any chlorides that may be brought into the cleaning solution.

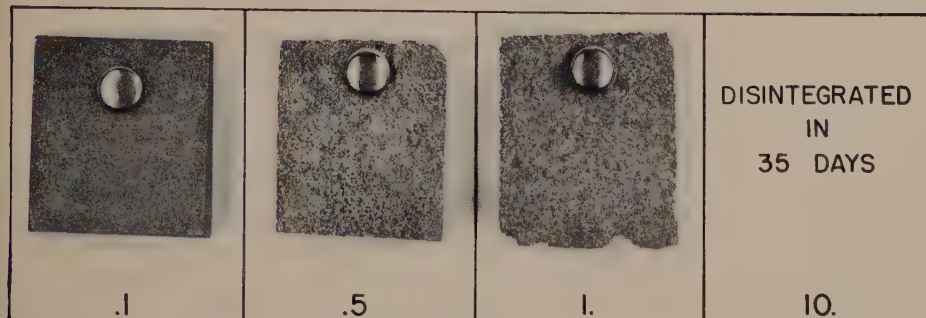
After the cleaning operation, washing in water and drying, the specimens were reweighed. From the determined weight loss, original areas and time of test, the corrosion rate was calculated as milligrams loss per square centimeter per day.

All specimens were examined visually not only to obtain information on the type of attack but to locate any extraordinary defects that might cause the quantitative results to be unreliable.

Fig. 2 is included to aid readers in obtaining a visual picture of the corrosion

corresponding to a certain numerical rate in milligrams per square centimeter per day.

corrosion rate. This phenomenon is described by saying that the tolerance limit of magnesium for iron is 0.017 per cent.



CORROSION RATE, MG. PER SQ. CM. PER DAY.

FIG. 2.—APPEARANCE OF SPECIMENS HAVING DIFFERENT CORROSION RATES AFTER 4 MONTHS ALTERNATE IMMERSION IN 3 PER CENT SODIUM CHLORIDE.

RESULTS

Graphical presentation of the results obtained in this work is used as an aid to an easy visualization of the corrosion data. As has been mentioned, commercial purity magnesium has widely varying corrosion rates within the range from 5 to 100 mg. per sq. cm. per day while high-purity magnesium has a rate of 0.15 ± 0.05 mg. per sq. cm. per day.

Fig. 3 gives a broad view of the corrosion of magnesium binary alloys with various common elements. While some elements are not harmful in large proportion, others are detrimental even when present in minute amounts. The present important alloy compositions come from combinations of the elements that are not harmful to corrosion. The common impurities in commercial magnesium alloys are iron, nickel, copper, lead and silicon. More detailed consideration of these impurities in the important magnesium alloys containing aluminum, manganese and zinc is then necessary. One begins with the study of iron, nickel and copper in magnesium. The results are shown in Figs. 4, 5 and 6 for iron, nickel and copper, respectively.

In amounts up to 0.017 per cent, iron has no effect on the corrosion rate of magnesium. Any excess of this quantity, however, causes a marked increase in

In Figs. 5 and 6, similarly, there is a sharp tolerance limit for nickel at less than 0.0005 per cent and for copper near 0.1 per cent.

The effect of the alloy elements manganese and zinc on the impurities iron, nickel and copper is seen in Figs. 4, 5 and 6, respectively, which show that in the cases of copper and iron the tolerance limit is unchanged though the increase in corrosion rate due to copper or iron above their respective tolerance limits is considerably reduced by the presence of about 1.0 per cent of manganese or zinc.

Fig. 5 shows that the tolerance of magnesium for nickel is greatly changed by manganese and is raised with increasing manganese content, being about 0.001 per cent nickel for 0.2 per cent manganese and about 0.015 per cent nickel for 2.0 per cent manganese. It also shows that zinc serves to raise the tolerance limit of magnesium for nickel.

While the use of 0.2 to 2.0 per cent manganese and of 1.0 to 1.5 per cent zinc appears arbitrary, these choices are indicated because these amounts correspond to those in common magnesium alloys.

A logical continuation of the experiments would be to show the effect of the presence of aluminum in magnesium on the tolerance limits for iron, nickel and copper. When one attempts to do this for iron he

gets results as shown in Fig. 7, in which it is shown that with even a very small content of aluminum the tolerance limit for iron has dropped from 0.017 per cent to

which gives a comparison of the results with 0.0 per cent manganese and 0.2 per cent manganese. With 0.2 per cent manganese the tolerance limit for iron does not

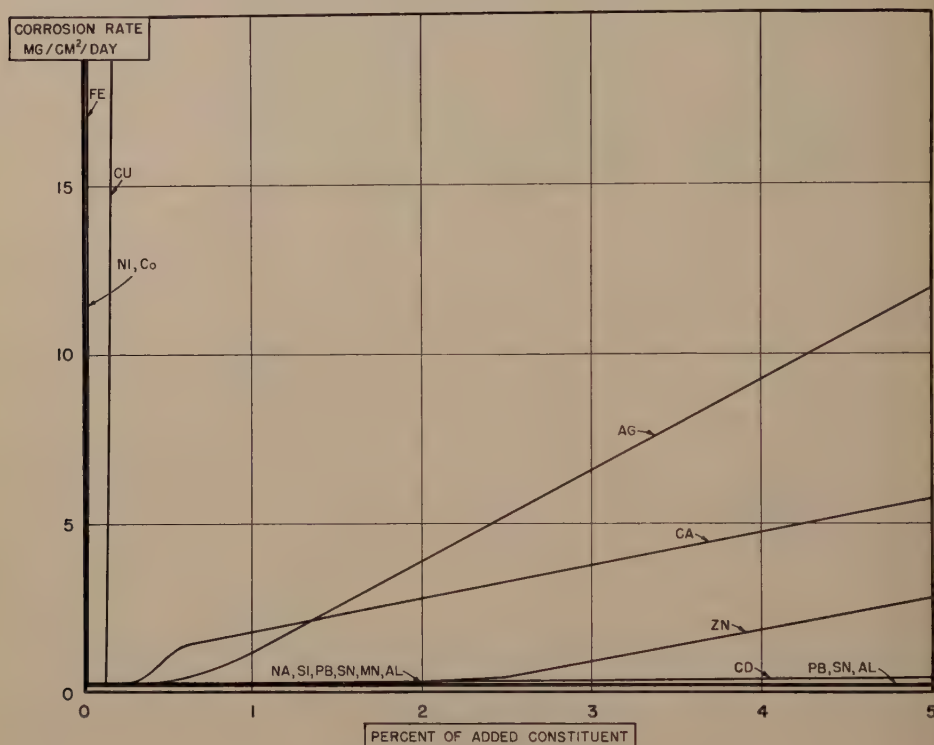


FIG. 3.—CORROSION OF MAGNESIUM BINARY ALLOYS.

a few thousandths per cent and that with 7.0 per cent aluminum it is about 0.0005 per cent. With 10.0 per cent aluminum, the limit is too low to be determined even though production and analysis can with sufficient care be carried to about 0.0002 per cent iron. Therefore, study of the tolerance limits of other impurities, such as copper and nickel, in the system magnesium-aluminum would be very difficult, since it would require practically nil iron.

It is only possible to proceed in a satisfactory manner by working with the system magnesium-aluminum plus a small amount of manganese. The action of this small amount of manganese is shown in Fig. 8,

drop below 0.002 per cent, but instead holds very constant over a wide range of aluminum content. A few hundredths per cent manganese is sufficient to give this effect.

Next comes the study of the impurities iron, nickel, copper in the magnesium-aluminum-0.2 per cent manganese system instead of in the magnesium-aluminum system.

The effect of aluminum with 0.2 per cent manganese on the impurities iron, nickel and copper in magnesium is shown in Figs. 9, 10 and 11, respectively. The aluminum content in the specimens indicated in these graphs varied in the range 2 to 12 per cent, with the great majority of the specimens

lying between 4 and 8 per cent. While the aluminum changes greatly, and in fact, is

that of the nickel probably not at all, since the 0.2 per cent manganese would account

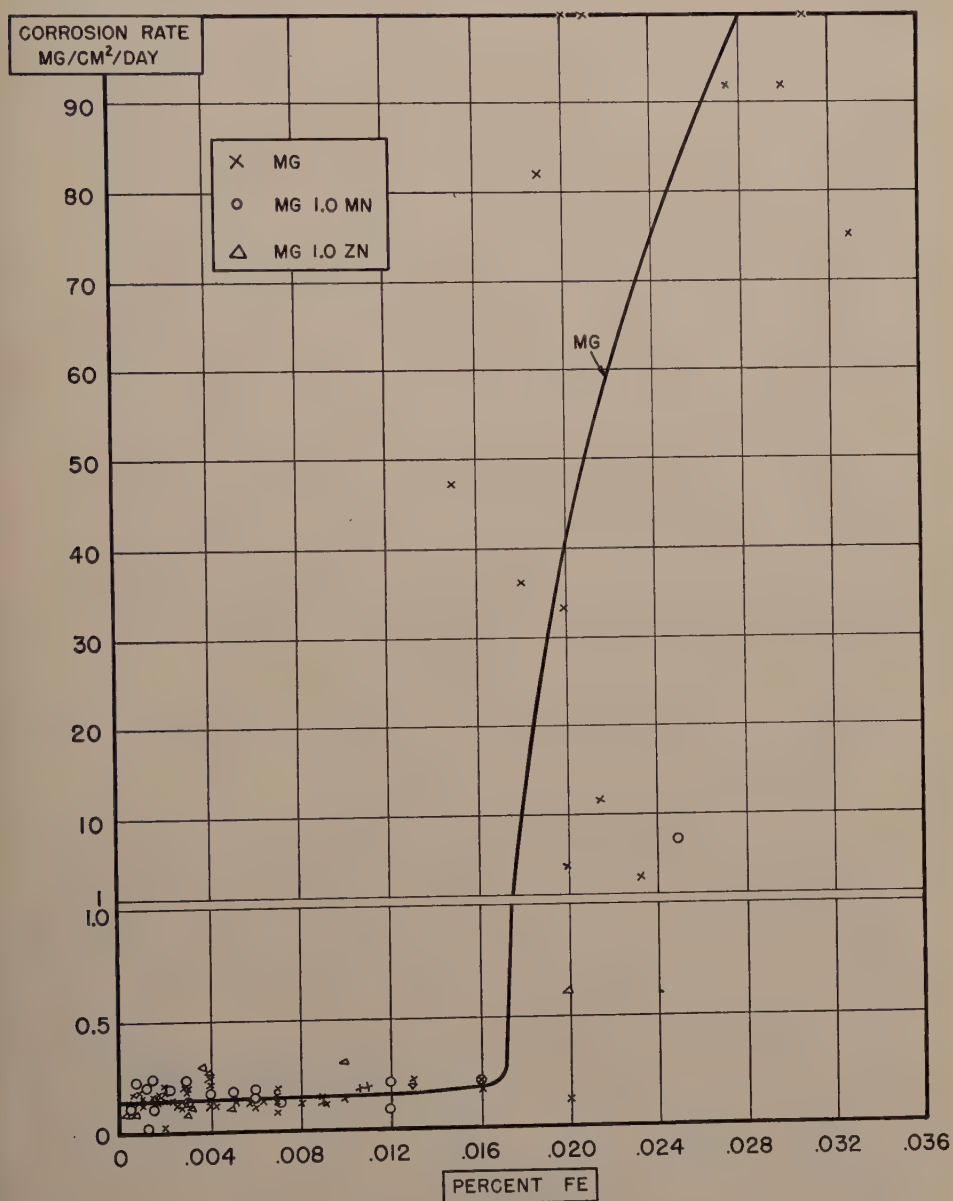


FIG. 4.—EFFECT OF IRON ON MAGNESIUM, MAGNESIUM-MANGANESE AND MAGNESIUM-ZINC.

the main determining factor of the position of the iron tolerance limit, it changes the position of the copper limit very little and

for the small shift from <0.001 per cent to 0.001 per cent nickel, which does take place. Since these large amounts of aluminum

have a negligible effect on the copper and nickel tolerance limits, it is unnecessary to

Since magnesium containing aluminum in the order of several per cent does not

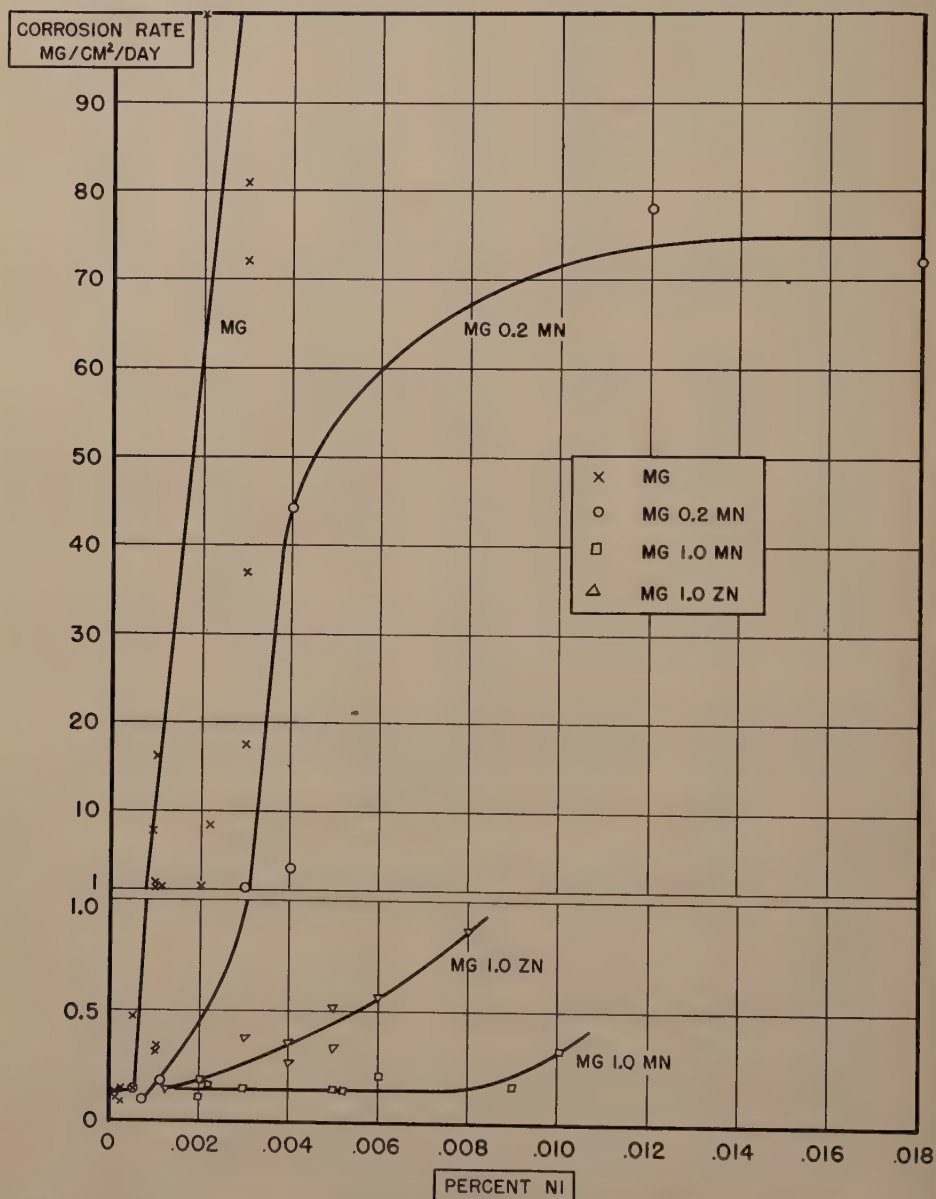


FIG. 5.—EFFECT OF NICKEL ON MAGNESIUM, MAGNESIUM-MANGANESE AND MAGNESIUM-ZINC.

study the effects over a wide range of aluminum, as was necessary in connection with iron.

dissolve more than a few tenths per cent manganese at the freezing point, one need not study the effects of more than this

percentage of manganese on magnesium-aluminum alloys.

Next, since zinc was effective in reducing

copper in the magnesium-aluminum-0.2 per cent manganese system must be studied.

Figs. 9, 10, and 11 show the results of

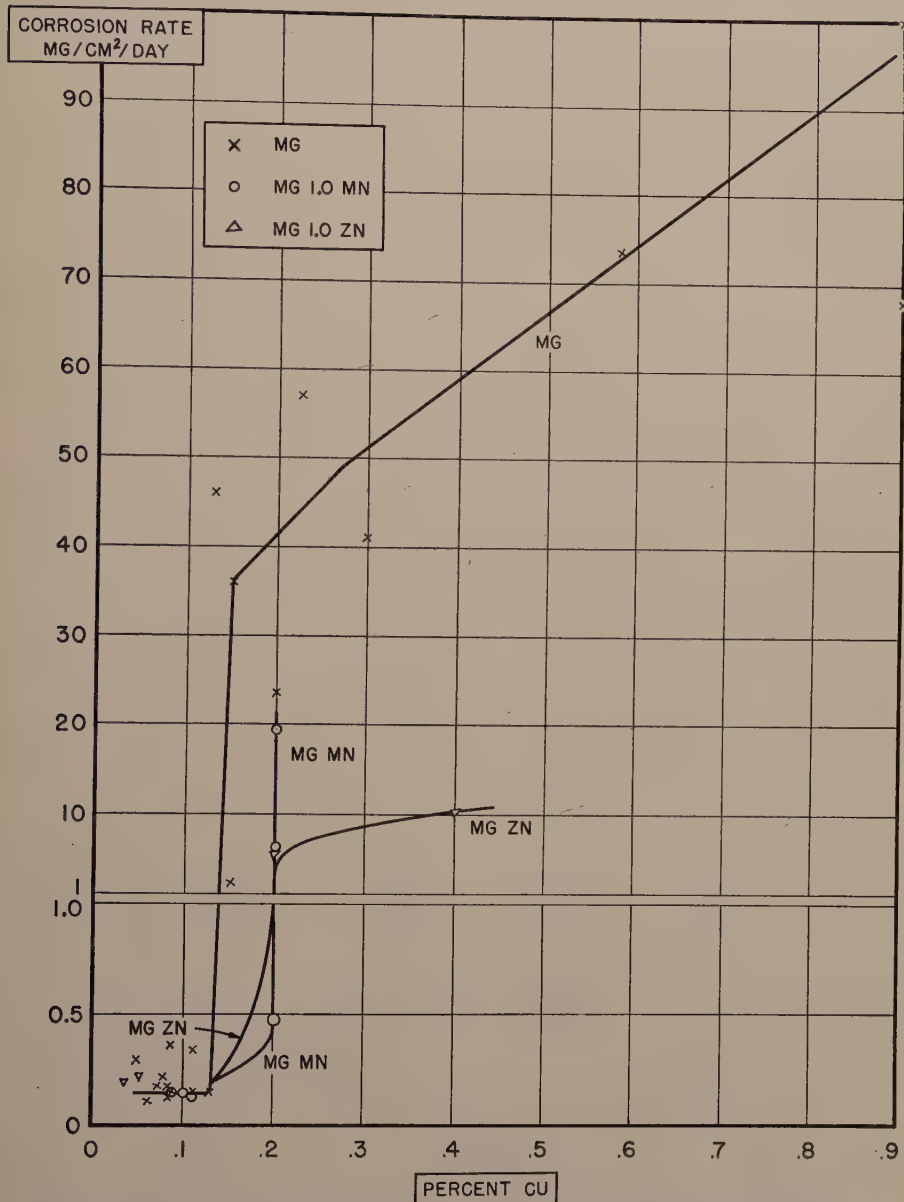


FIG. 6.—EFFECT OF COPPER ON MAGNESIUM, MAGNESIUM-MANGANESE AND MAGNESIUM-ZINC.

the harmful effects of iron, nickel and copper in magnesium, its action on iron, nickel and

adding 0.5 and 3 per cent zinc to the magnesium-aluminum-0.2 per cent manganese

alloys. Fig. 9 shows that 0.5 per cent zinc does not shift the position of the iron tolerance limit at 0.002 per cent, but somewhat reduces the magnitude of the corrosion rates

magnesium-aluminum-manganese-nickel alloys, 3 per cent zinc has shifted the tolerance limit from 0.001 to 0.002 per cent nickel and greatly reduced the corrosion

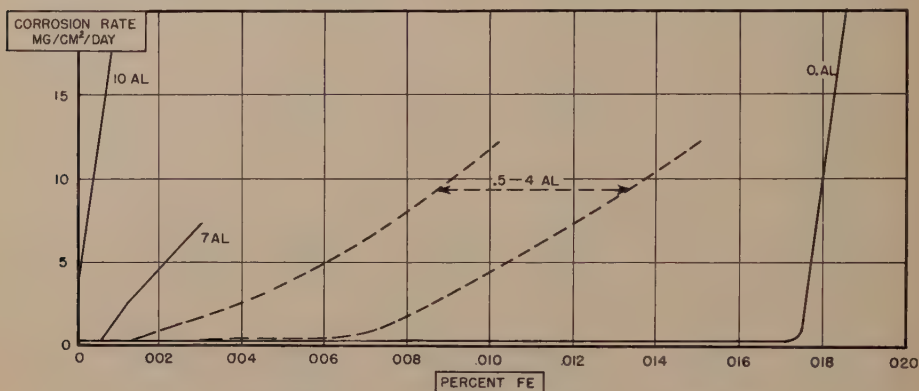


FIG. 7.—CORROSION OF MAGNESIUM-ALUMINUM CONTAINING IRON.

for higher percentages of iron. However, addition of 3 per cent zinc gives an interesting result in that the tolerance limit is raised to 0.003 per cent iron and the corrosion rate greatly reduced for higher per-

rate at higher percentages of nickel. Fig. 11 shows that 0.5 per cent zinc raises the copper tolerance limit only slightly whereas 3 per cent zinc raises it to at least 0.5 per cent copper.

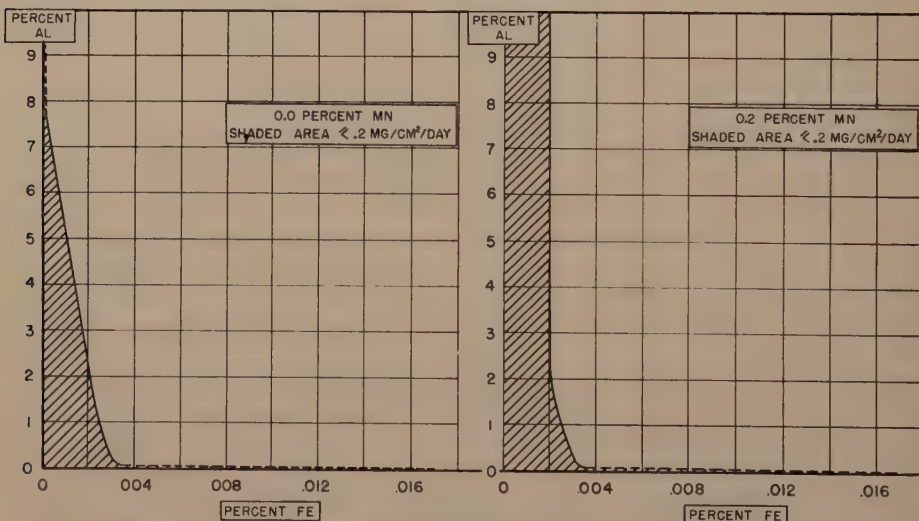


FIG. 8.—EFFECT OF MANGANESE ON THE IRON TOLERANCE OF MAGNESIUM-ALUMINUM.

centages of iron up to 0.012, at which point a gradual increase of corrosion rate begins. Fig. 10 shows that while 0.5 per cent zinc has little effect on the corrosion behavior of

These data serve to show that the magnesium alloys studied are characterized by tolerance limits for iron, nickel and copper when present singly in the alloys.

It remains to show the results when the impurities are simultaneously present.

on the contrary, there exists an interaction of some or all of them, which would result

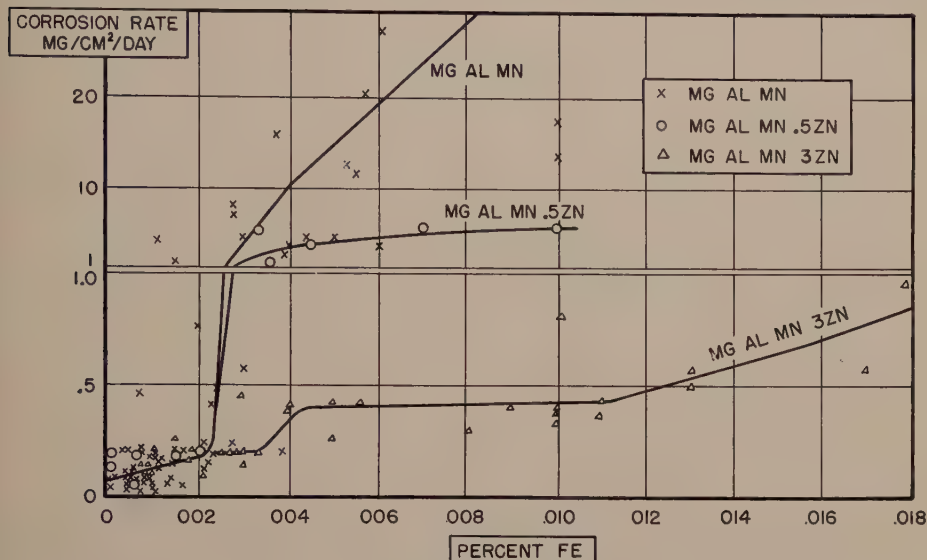


FIG. 9.—EFFECT OF IRON ON MAGNESIUM-ALUMINUM-MANGANESE AND MAGNESIUM-ALUMINUM-MANGANESE-ZINC.

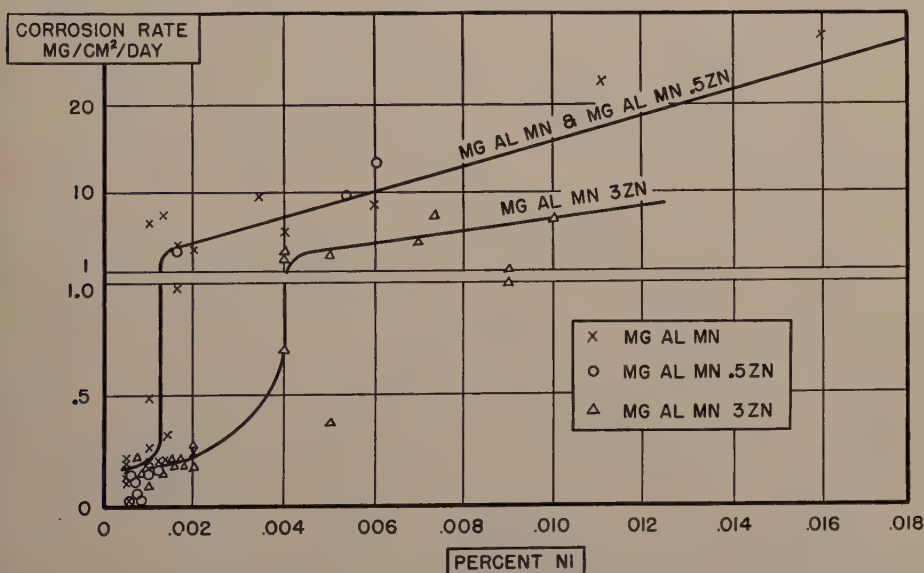


FIG. 10.—EFFECT OF NICKEL ON MAGNESIUM-ALUMINUM-MANGANESE AND MAGNESIUM-ALUMINUM-MANGANESE-ZINC.

Without experimental work it could not be known whether some of the elements counteract the effects of others or whether,

in a lowering of the tolerance amounts as determined for the individual elements. As evidence of these possibilities, it is

pointed out that 0.01 per cent aluminum greatly increased the sensitivity to iron while 0.02 per cent manganese, on the other hand, was very effective in counteracting

alloys in which the impurities somewhat exceeded their tolerance amounts.

A study of this second group of alloys showed that there were no cases having

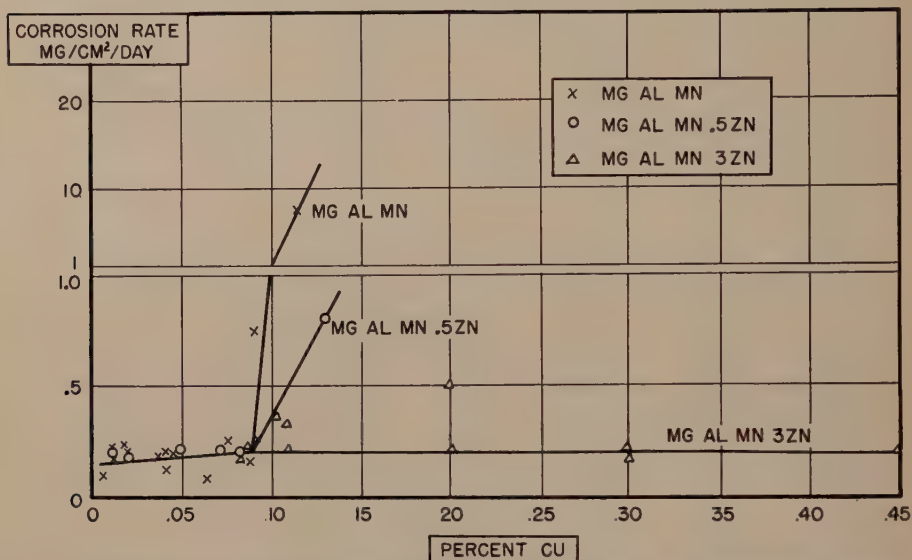


FIG. 11.—EFFECT OF COPPER ON MAGNESIUM-ALUMINUM-MANGANESE AND MAGNESIUM-ALUMINUM-MANGANESE-ZINC.

the corrosive effect of iron. Thus even extremely small amounts of certain elements may result in striking changes in the corrosive effects of other elements.

Further, in order to make the results of practical importance, one must study not only the combinations of the known harmful impurities, iron, nickel and copper, but must include as well the common impurities silicon and lead, even though separately silicon and lead cause no corrosion, though present in amounts 10 times as great as their normal amounts in commercial alloys.

In order to answer these questions, the corrosion rates were studied for a group of magnesium-aluminum-manganese alloys in which two or more of the elements iron, nickel, copper, silicon and lead were present—none, however, being present in excess of its tolerance limit as determined individually—and also for a second group of

observable counteracting effect on the corrosive action of any of the impurities.

From the study of the first group, however, it was found that definite interaction existed for combinations of iron with copper, lead or silicon. These combinations were then studied in detail, with the results as shown in Figs. 12, 13 and 14.

The significance of the boundary lines drawn on Figs. 12, 13 and 14 is that within these lines corrosion rate does not exceed 0.2 mg. per sq. cm. per day while outside of these lines the rate is greater than 0.2 and therefore greater than the rate for high-purity magnesium. This means that the compositions outside the lines have a detrimental effect on the corrosion resistance. Difficulties due to analysis and uniformity of composition of these specimens were greater than when only one impurity was being studied, and this accounts probably for the failure of the

points to determine a more precise location of the boundary line. Nevertheless the points give strong evidence of the existence of the areas substantially as shown.

technique. Alloys of magnesium, magnesium plus 3 per cent aluminum and magnesium plus 3 per cent aluminum plus 0.05 per cent manganese were made with vary-

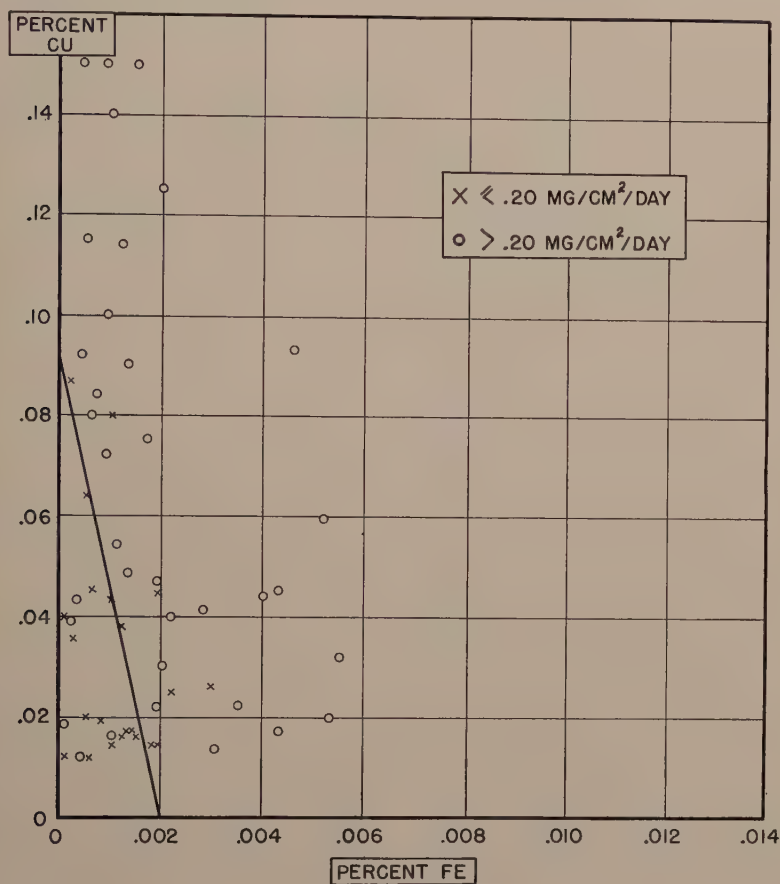


FIG. 12.—CORROSION OF MAGNESIUM-ALUMINUM-MANGANESE CONTAINING IRON AND COPPER.

When 3 per cent zinc is added to magnesium-aluminum-manganese alloys, no evidence for interactions of the type shown in Figs. 12, 13 and 14 can be detected.

METALLOGRAPHIC EXAMINATION

METHOD

The alloys for metallographic study were prepared from high-purity magnesium and pure alloying materials in a uniform manner as regards alloying and pouring

ing amounts of the single impurities iron, nickel and copper in such proportions as to cover a range from substantially zero to well above the tolerance limit for that specific impurity in each of the basic compositions mentioned. Two types of castings were made, one sand-cast in a standard tensile mold, the other chill-cast in a graphite mold of $\frac{1}{2}$ by $\frac{1}{2}$ -in. cross section. Samples for study were cut from the same place on each casting in such a way as to present an average cross section. Most of the com-

parative data were taken from observations on the chill-cast samples. However, examinations were also made of the sand-cast

3. Final wet polishing on a similar wheel covered with velvet, using a distilled-water suspension of relevigated alumina.

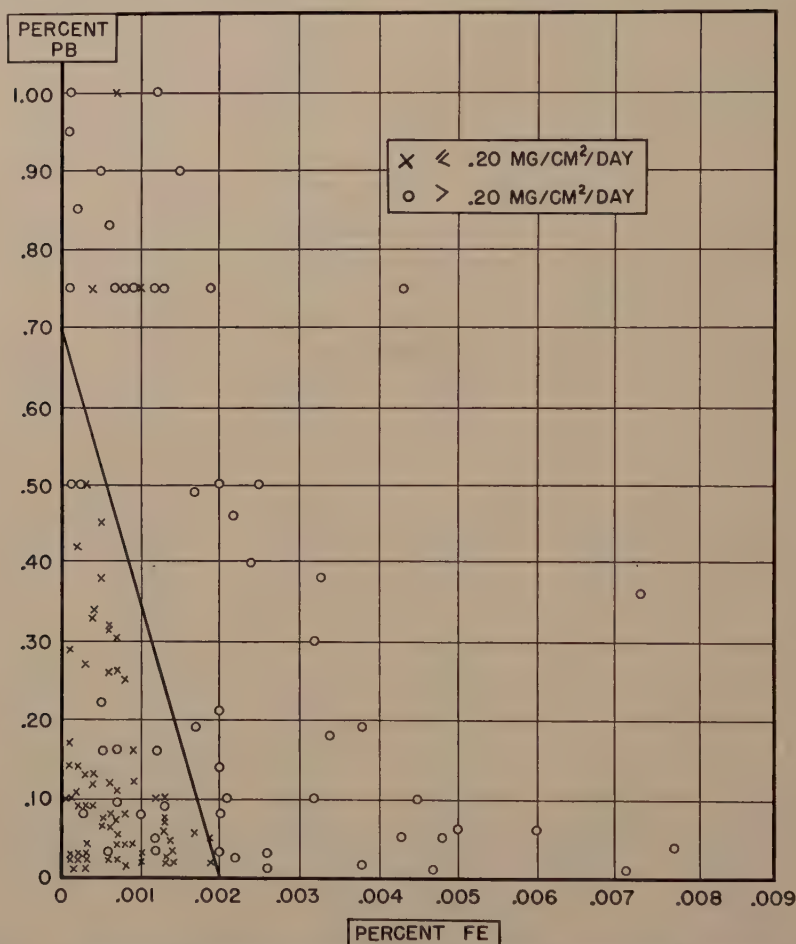


FIG. 13.—CORROSION OF MAGNESIUM-ALUMINUM-MANGANESE CONTAINING IRON AND LEAD.

samples, in order to check the effect of the rate of chill.

The specimens for metallographic examination were prepared by the following steps:

1. Rough grinding up through 000 French emery paper.

2. Wet polishing on a horizontal rotating wheel covered with Vel-Chamee cloth, using a distilled-water suspension of No. 600 alundum.

4. Etching to bring out the various constituents, as will be discussed in more detail later.

RESULTS

While examination of the samples in the as-polished state indicated the presence of some of the impurities, it was found necessary to evolve an etching technique for each element in order to obtain positive identification. In samples containing iron,

particles of the iron phase can be seen in the as-polished condition, but more positive identification depends on the fact that exposure to ordinary tap water for a few

be allowed to take place while the specimen is under observation with the microscope. Gas can be seen to be evolved slowly from the particles, accompanied by

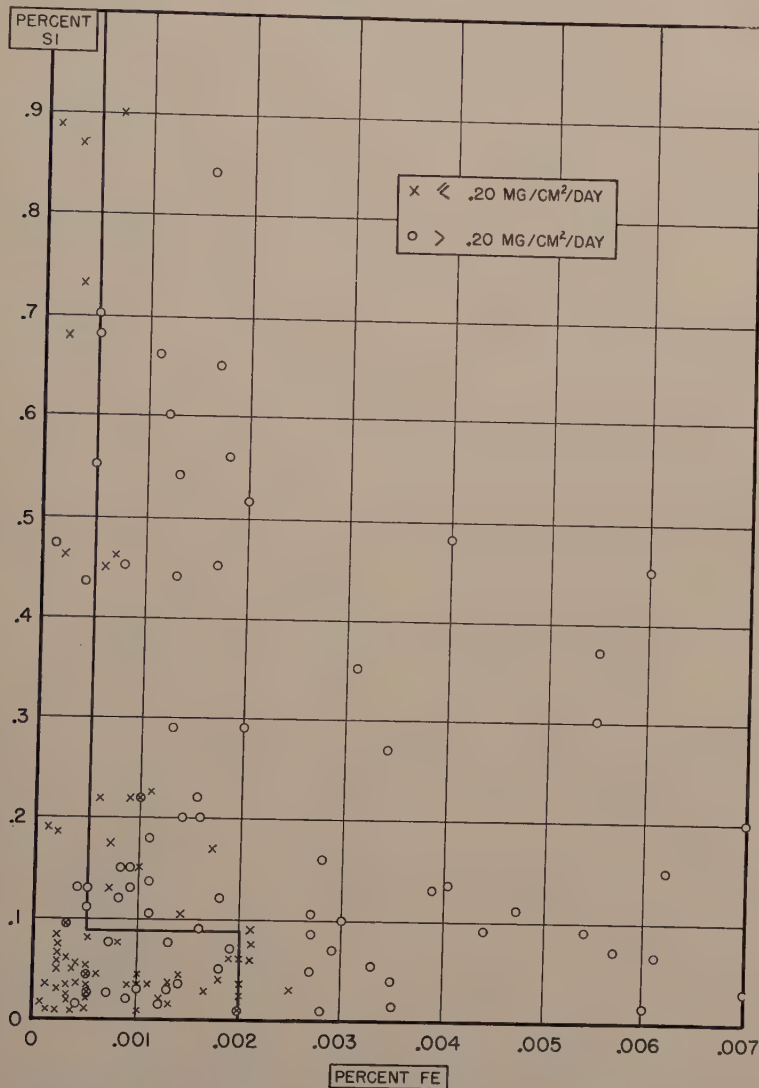


FIG. 14.—CORROSION OF MAGNESIUM-ALUMINUM-MANGANESE CONTAINING IRON AND SILICON.

seconds causes a dissolution of the magnesium-rich matrix around the iron particles, as is indicated by the appearance of broad circles around the inclusions. Longer attack by tap water or salt solution may

gradual broadening of the anodic areas surrounding them. Actual counts of the number of iron particles in a standard area of the various specimens indicate the number of particles to be approximately

proportional to the iron content. Some of these facts have also been noted by Vosskühler.⁴ In comparing the number of particles in a magnesium-iron alloy with that for a magnesium-3 per cent aluminum-iron, one finds that at 0.001 per cent iron no particles can be seen in the magnesium-iron whereas a number can be seen in the magnesium-3 per cent aluminum-iron. At their respective iron tolerance limits, 0.017 and 0.002 per cent iron, the two alloys appear to contain approximately the same number of particles, but the particles in the magnesium-iron are somewhat smaller. One further observation of interest is that the particles have a random distribution and tend to segregate in varying degree through the samples. Although a determination with any degree of accuracy is difficult, it is roughly estimated that the particle diameter of the iron constituent at the tolerance limit is of the order of 0.00001 in., while the average distance between particles is about 0.0001 to 0.0005 inch.

In copper-containing magnesium, the compound Mg_2Cu can be detected by etching in a solution of 74 per cent diethylene glycol, 25 per cent water and 1 per cent HNO_3 . In a specimen containing 0.05 per cent copper the Mg_2Cu compound is almost entirely in the grain boundaries, whereas if 0.10 per cent copper or over is present the Mg_2Cu compound is not only in the grain boundaries but also a great number of particles appear throughout the matrix.

For magnesium and its alloys containing nickel, it is possible to use the glycol etch to reveal the nickel phase. Although only a little work has been done thus far, it is worthy of note that a magnesium-nickel compound can be seen in the grain boundaries at nickel contents as low as 0.0005 per cent.

SOLUTION POTENTIAL AND HYDROGEN OVERVOLTAGE MEASUREMENTS

In order to aid in the test of the applicability to the corrosion results of any

accepted electrochemical theories, some measurements of solution potential and hydrogen overvoltage are included. The measurements were made in 3 per cent NaCl under the conditions used for the corrosion tests, with the hope that some correlation of results would be possible. Unfortunately, the electrochemical measurements are not complete enough at the moment to cover the behavior of magnesium-base alloys as a function of varying impurity content, and therefore do not aid in an explanation of the existence of the sharp discontinuities or tolerance limits. However, data are presented to show why certain elements are detrimental to the corrosion resistance of magnesium.

METHOD

[Preparation of Samples]

Magnesium-alloy electrodes were ground to a size of 0.5 by 0.5 by 5 cm. on aluminum oxide abrasive paper, the final cut being made with No. 320 grit. The samples were not handled after grinding, since grease delayed the attainment of a steady potential. The shape of other metal electrodes used in the tests depended somewhat on the samples available. The surface preparation was the same as for magnesium alloys.

Measurement of Electrode Potentials

The electrode potentials were measured with a Leeds and Northrup special wide-range type K potentiometer, using a Weston unsaturated cell as standard. The potentials were measured in the cell metal: 3 per cent NaCl; saturated calomel electrode at 25.0°C. Precautions were taken to prevent diffusion at the liquid boundary, and frequent checks of the working calomel electrode against a reference gave differences never exceeding 0.0002 volt. Each electrode was observed for a period of at least 24 hr. In all cases a steady potential was achieved after 12 hr. Once a steady potential had been achieved, it remained constant in most cases to

within ± 0.005 volts as long as observed (maximum 48 hr.). A few electrodes varied by ± 0.01 volt in 48 hours.

Measurement of Hydrogen Overvoltages

Hydrogen overvoltage, defined as the negative potential that must be applied to an electrode to liberate hydrogen at a specified current density, was measured by passing a current through the electrolytic cell: metal cathode: 3 per cent NaCl platinum anode and measuring the increase in potential of the metal electrode above the zero current value, with respect to the saturated calomel electrode. The overvoltages used in the calculations were measured at a current density of 5 ma. per sq. cm. Since the relative values are essentially independent of current density, this choice is somewhat arbitrary.

RESULTS

Some results that seem to be of particular interest are given in Table I.

ELECTRON DIFFRACTION PATTERNS OF SURFACES

The nature of the protective film formation on the surfaces of metals is recognized to be an important factor in metallic corrosion. The possibility exists of obtaining some information about the structure of such films directly by means of electron diffraction if the films happen to be in a sufficiently crystalline state.

METHOD

The compositions studied included Mg, Mg-6Al, Mg-1Mn, Mg-6Al-0.2Mn, Mg-4Al-3Zn-0.2Mn. The specimens had previously been exposed to dry air, distilled water, 3 per cent NaCl solution, and other treatment. A specially high dispersion and resolution was obtained in these patterns by using a distance from specimen to photographic plate of 72.3 ± 0.1 cm. and by controlling the high potential supply of minus 40 kv. to within ± 3 volts. The

electron-beam pinhole diaphragm was 0.25 mm. and the pinhole to lens distance was 75 cm. The surface of the specimen covered by the convergent electron beam was 0.7 by 1.0 centimeter.

TABLE I.—Values of Solution Potential and Hydrogen Overvoltage Determined in 3 Per Cent Sodium Chloride

Composition ^a	Solution Potential	Hydrogen Overvoltage
Mg.....	1.70	0.64
Mg-0.02Fe.....	1.57	0.02
Mg-3Al.....	1.76	0.66
Mg-45Al (Mg ₄ Al ₅).....	1.24	0.52
Mg-63Al (Mg ₂ Al ₃).....	1.23	0.70
Al.....	1.06	0.79
Mg-1.1Mn.....	1.70	0.35
Mn.....	1.27	0.39
Mg-1.2Zn.....	1.73	0.25
Mg-73Zn (Mg ₂ Zn) ¹	1.27	0.34
Mg-84Zn (Mg ₂ Zn ₂).....	1.09	0.53
Zn.....	1.06	0.39
Mg-57Cu (Mg ₂ Cu) ¹	1.01	0.13
Mg-84Cu (MgCu ₂).....	0.91	0.34
Fe.....	0.73	0.56
Fe-59Al (FeAl ₃).....	0.72	0.35
Co.....	0.50	0.71
Mg-55Ni (Mg ₂ Ni) ¹	0.92	0.05
Ni.....	0.15	1.02
Mg-2Ag.....	1.64	0.17
Mg-82Ag (MgAg) ¹	0.25	1.19

^a Magnesium and magnesium-base alloys listed are of high purity.

RESULTS

The results of the electron diffraction study were negative in that they failed to show any substantial difference in the patterns as a function of the composition of the alloy. In dry air at room temperature the result was a diffuse MgO pattern. In aqueous media at room temperature the result was the pattern of Mg(OH)₂, though with relative intensities of the lines differing from those of bulk Mg(OH)₂, and with indications of slight variations in line positions. These intensity variations are probably related to orientation effects, but will require further study, as will also the other differences observed. The published literature on electron diffraction studies of magnesium structures also gives evidence for anomalous structures.^{5,6}

Visual observations of the protective film formed in aqueous media on magnesium alloys with aluminum in the range

up to 10 per cent plainly show that the film is thinner the higher the aluminum content of the alloy, and therefore strongly indicate that the chemical or physical nature of the film is different, depending on the percentage of aluminum in the alloy.

It has been stated in the literature⁷ that the protective coat on manganese-containing magnesium alloys is manganous hydroxide at least in substantial part.

The electron diffraction results reported do mean that $\text{Mg}(\text{OH})_2$, or $\text{Mg}(\text{OH})_2$ modified slightly, is a major part of the film, independent of the alloy composition within the range of composition covered. They should not be interpreted to mean that the film action is not greatly determined by the presence of aluminum or manganese compounds, since these may be amorphous or for other reasons may not be detected by electron diffraction.

DISCUSSION OF RESULTS

Probably the most extensive discussions in the literature on the corrosion behavior of magnesium are by W. Schmidt and W. Schultze⁸ and by W. Schultze.⁹ These are excellent articles and devote considerable space to the effects of metallic impurities in magnesium. They do not, however, make a study in sufficient detail to bring out the critical relationships presented in the present paper, so no very direct comparison of results is possible.

It is commonly accepted¹⁰⁻¹² that the corrosion of magnesium in salt solutions is entirely electrochemical in nature, the sole cathodic reaction being the evolution of hydrogen gas, the anodic reaction consisting of the passage of Mg^{++} ions into solution with subsequent reaction with OH^- ions to form $\text{Mg}(\text{OH})_2$ or perhaps the direct formation of $\text{Mg}(\text{OH})_2$ on the surface of the metal by the discharge of OH^- ions. Constituents nobler than magnesium present as a second phase in the magnesium should act as cathodes for local corrosion

cells. One might then logically look for an explanation for the tolerance limits in terms of the limits of solubility in the alloy for the constituent concerned. This may possibly be the explanation for the tolerance limit of magnesium for copper at about 0.1 per cent. Metallographic examination shows that copper is soluble to a small degree in magnesium.¹³⁻¹⁶ It is soluble to about 0.2 per cent at 400°C. and the solubility drops with temperature to something less than 0.05 per cent at room temperature. In the as-cast metal, which is the state used for the corrosion tests, there appears a precipitate of the copper phase in large quantities for copper contents of 0.1 per cent or greater.

Examining the case of iron, which in magnesium has a tolerance limit at 0.017 per cent, it is found that the limit of solubility in molten magnesium at the freezing point is slightly under 0.02 per cent. However, in the solid state, metallographic examination shows iron to be insoluble down to at least a few thousandths per cent. The numbers of iron-phase particles (which occur within the grains) that can be counted in the microscope are proportional to the iron content of the magnesium. *Thus it is certain that the solid solubility limit and the tolerance limit do not correspond in this case.* Further studies may show whether the liquid magnesium solubility limit is of any significance in relation to the tolerance limit.

For magnesium-aluminum alloys and magnesium-aluminum-manganese alloys, the solubility of iron in the liquid state is appreciable at high temperatures but is less than 0.001 per cent iron at the freezing point. The iron solubility in solid magnesium-aluminum or magnesium-aluminum-manganese is also very low. Metallographic examination shows the particles of the iron phase to be present at as low as 0.0005 per cent iron. *Therefore the tolerance limit at 0.002 per cent iron does not correspond to any solubility limit in these alloys.*

The iron particles appear to be in random distribution, the concentration of particles being higher at some places and lower at others. This agrees with the results of chemical and spectrographic spot analyses, which also were able to show segregation of iron in these alloys. It is of interest to note that on the average the number of particles of iron phase per unit of surface observed in magnesium at 0.017 per cent iron or in magnesium-aluminum at 0.002 per cent iron is approximately the same, while the number of iron-phase particles in magnesium at 0.002 per cent iron appears to be only a very small fraction of the number in magnesium-aluminum at 0.002 per cent iron. The particles are very small and, at the percentage corresponding to the tolerance limit, are separated at distances estimated to be of the order of magnitude of 0.0001 in. Presumably the composition of the particles in magnesium is iron, while in magnesium-aluminum or magnesium-aluminum-manganese the composition is FeAl_3 or some more complicated substance.

An explanation might be found for the great increase in corrosion resulting from only a small increase in the number of particles beyond a certain critical number in that up to this critical number the corroding spots are isolated and do not contact or expose new particles, but that beyond this number the particles are close enough together so that the corrosion caused by the particles exposes new particles to the corroding medium. This theory assumes that each particle causes a definite amount of dissolution of magnesium but does not need to make any assumption about the mechanism by which the corrosion due to the particle is stopped after a definite amount of corrosion has taken place. For specimens with iron below the tolerance limit, the fact mentioned previously, that there are random segregations or regions of higher concentration of particles, accounts for the observation that there may be localized areas of visible

corrosion in such specimens. The iron at such places was found by special analysis to be above the tolerance limit. The conception of a specimen with impurity above its tolerance limit is, then, that for such a specimen the regions of higher concentration are so numerous that they touch each other and cover the surface, or perhaps, said more simply, the impurity concentration is such that the tolerance limit is exceeded at every point. Specimens with average impurity below the tolerance limit may, and do, have isolated areas in which the average impurity content for these areas exceed the tolerance limit.

Further hypotheses would be necessary to predict the absolute magnitude of the tolerance limit for any particular case. Since the particles do not touch each other (as do the base atoms in the "critical resistance limits" of Tammann) but rather, for example, in iron inclusions, appear to be of the order of 10 to 100 times their diameter apart in the neighborhood of the critical concentration, the absolute magnitude of the critical concentration depends upon the extent of corrosion caused about each particle. Probably corrosion continues until the particle is removed by undermining itself. This is the simplest and most plausible theory and has confirmation in the experiments on metallography and spot analysis of corroded areas.

As has been shown by the measurements of solution potentials and hydrogen overvoltage, the particles of impurity serve as cathodic points, which permit the evolution of hydrogen gas. It is possible that there exists a critical anodic current density below which protective film formation takes place but above which corrosion can continue. The nature of the film that forms, and the critical value of the anodic current density that will permit the film to form, should both be functions of the composition of the alloy. The magnitude of the anodic current density is governed by the amount of hydrogen gas that can be evolved at

cathodic areas. The larger the ratio of cathodic area to anodic area, the smaller the distance between these areas and the higher the conductivity of the electrolyte and of the surface film, the greater will be the amount of hydrogen evolved. As discussed later, it should be a function of the "driving force" measured by the excess of the difference in solution potentials between anodic and cathodic areas over the hydrogen overvoltage of the cathodic area.

If corrosion is stopped by film formation, it may be necessary not only for the film to form over the anodic area but to be able to grow over and shut off or "strangle" the cathodic areas. It is only when polarization at the cathodic area is accomplished at negligible current that corrosion can be said to have ceased. Thus one may be concerned not only with a critical anodic current density that allows film formation but with a critical size of cathode areas, which the anodic film is capable of shutting off.

The following experiment can be interpreted as evidence for the existence of a critical value of current density as discussed above. If a magnesium-alloy specimen with all impurities below their tolerance limits is placed in salt solution, there is an evolution of hydrogen from the specimen while film formation is taking place. Visible gas evolution soon stops and film formation is presumably complete. If a new cathodic area that can evolve hydrogen is connected to the specimen, a high current flows, but not only to the new cathode. Hydrogen also begins to evolve from the specimen again and will continue to do so until the external cathode is removed; that is, protective film formation makes no headway as long as the additional current is flowing. As soon as the external cathode is removed, protective film formation begins again and soon stops the hydrogen evolution from the local cathodic areas. This experiment serves to emphasize that the film on the anodic areas did not prevent

corrosion while there existed any areas on which hydrogen could evolve. Boyer¹⁷ and Vyskocil¹⁸ have discussed the cause of the breakdown of the anodic film in terms of a "catalytic" effect of chloride ions.

Considerably more work will be necessary to aid in choosing between the various speculations on the explanation of the characteristics of the tolerance-limit phenomena. The simpler question of why some elements act in the direction of accelerating the corrosion of magnesium in salt solution while others do not can be explained in terms of electrochemical properties. The figures in Table 2 have been derived from the experimentally measured values given in Table 1 by taking the difference between the solution potentials of magnesium and of the material in question and then subtracting the hydrogen overvoltage of the material in question. This is done on the assumption that this quantity is some measure of the driving force tending to evolve gaseous hydrogen at the cathodic spot. For elements that have solid solubility in magnesium, the solution potential of the phase that would be precipitated should be subtracted from the solution potential of the solid solution phase instead of from the solution potential of magnesium.

Table 2 shows that for aluminum, manganese and zinc there is either no resultant driving force or only one of about 0.1 volt, while for iron, cobalt, copper and nickel the driving force is greater than 0.4 volt. Silver shows an intermediate position at 0.21 volt. Thus the value of the quantity P.D.-O.V. serves to correctly classify each metal observed according to its corrosive action on magnesium. It is to be noted that there is no correlation of corrosion effect with hydrogen overvoltage.

It is stated by Gatty and Spooner¹⁹ that the hydrogen overvoltage of magnesium is very low, and a part of their discussion is based upon this claim. Table 1 shows that the overvoltage of pure magnesium is high but is greatly lowered by iron. From the

analysis for magnesium given in their paper, it can be seen that their determined overvoltage for magnesium was in error because of the presence of iron in their specimen.

TABLE 2.—*Difference in Solution Potentials and Overvoltage Values for Various Types of Cells*

Anodic Material	Cathodic Material	Difference in Solution Potentials (P.D.), Volts	Hydrogen Overvoltage of Cathodic Material (O.V.), Volts	P.D.-O.V., Volts
Mg-3Al.....	Mg ₃ Al ₃	0.52	0.52	0
Mg-3Al.....	Mg ₂ Al ₃	0.53	0.70	-0.17
Mg-1.1Mn.....	Mn	0.43	0.39	0.04
Mg-1.2Zn.....	MgZn	0.46	0.34	0.12
Mg-1.2Zn.....	MgZn ₂	0.64	0.53	0.11
Mg.....	Mg ₂ Cu	0.69	0.13	0.56
Mg.....	MgCu ₂	0.79	0.34	0.45
Mg.....	Fe	0.97	0.56	0.41
Mg-3Al.....	FeAl ₃	1.04	0.35	0.69
Mg.....	Co	1.20	0.71	0.49
Mg.....	Mg ₂ Ni	0.78	0.05	0.73
Mg-2Ag.....	MgAg	1.39	1.19	0.20

The results published by Boyer¹⁷ show that while his magnesium specimens were pure enough for studies of magnesium metal, they were not of sufficient purity to use as a base for aluminum-containing alloys, and this accounts for many of the discrepancies between his results and those of the present paper. Schultze⁹ has made valuable contributions to the subject of the corrosion behavior of magnesium and has given careful consideration to the effects of small amounts of impurities in magnesium. However, his publications contain corrosion results that are presumed to be characteristic of magnesium and alloys but that obviously are influenced by impurities.

It seems fair to say that many of the results reported in the literature on the corrosion of magnesium and its alloys are not representative of the basic nature of the metal but are determined by the presence of uncontrolled or insufficiently controlled metallic impurities, which were regarded as negligible. It would be well if

all published results were critically examined from this point of view.

PRACTICAL ASPECTS

While for purposes of establishing the fundamental factors governing corrosion behavior of magnesium and its common alloys it is necessary to begin with very pure or sublimed magnesium and to keep every element nil except the ones under investigation, this is not necessary for purposes of producing good corrosion-resistant magnesium alloys in practice. The present high grade of ingot magnesium available commercially in the United States can be used as a base for such corrosion-resistant alloys simply by making use of the insolubility of iron as previously described, giving due regard to selection of materials and exercising adequate precautions in handling.

It is interesting and important to note that in the past, for certain alloys, the effects of some impurities have been over-emphasized, whereas the data presented show that these impurities may really be present in amounts in excess of the usual specifications without detrimental effect on corrosion stability. For example, the commercial specifications on Mg-6Al-Mn-3Zn limit copper to 0.05 per cent while 0.5 per cent would be allowable as far as corrosion is concerned.

Alloys with impurities below the tolerance limits have been produced on commercial scale in the form of sand castings, die castings and wrought shapes. The corrosion rates on these alloys are less than 0.2 mg. per sq. cm. per day. Tests of the loss in tensile properties due to corrosion have been carried out on standard test bars of some common Mg-Al-Mn-Zn alloys with the results as shown in Fig. 15. There are only minor losses in properties over a period of 180 days in salt solution for cast alloys, though alloys in the wrought form are somewhat more sensitive.

SUMMARY OF RESULTS

1. The basic nature of magnesium and of its important alloys is that they are very resistant to salt-water corrosion but are

the hydrogen overvoltage of the cathodic material.

5. On the basis of metallographic and other types of examination, an assumption

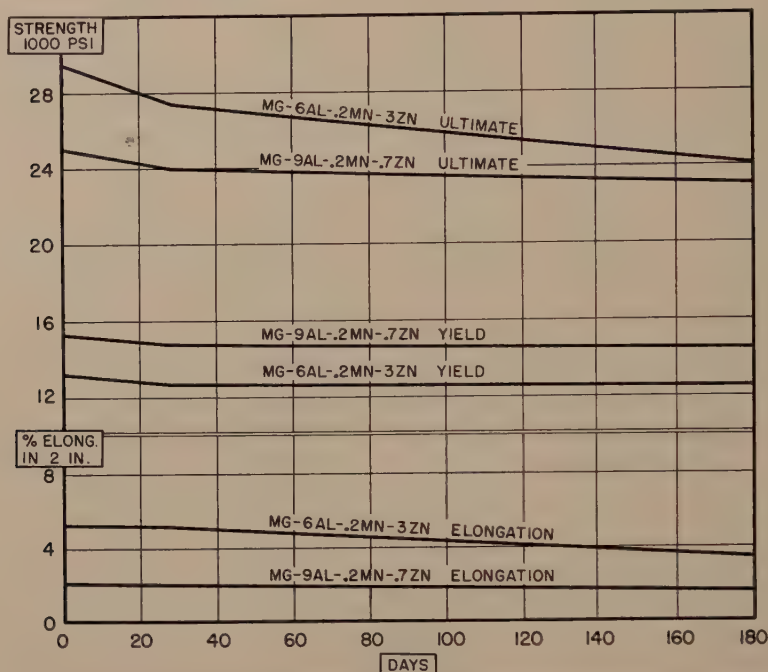


FIG. 15.—CORROSION-TENSILE PROPERTIES OF CAST MAGNESIUM-ALUMINUM-MANGANESE-ZINC.

extremely sensitive to certain elements and combinations of elements.

2. The specific effect on the salt-water corrosion resistance of magnesium due to the elements aluminum, manganese, zinc, iron, nickel, copper, silicon and lead singly and in all combinations has been determined.

3. The existence of "tolerance limits" or discontinuities in the rate of corrosion as a function of the percentage present of certain elements has been demonstrated.

4. It is shown that the elements studied can be classified in their gross effect on the corrosion resistance of magnesium according to the excess of the difference in solution potentials of the magnesium or anodic material and of the cathodic material over

of a critical concentration of cathodic particles is used to explain the origin of the corrosion discontinuities.

6. Alloy compositions that meet the purity requirements for good corrosion stability, and which represent the range of commercial usage, have been prepared on production scale in the form of ingots, sand castings, die castings and wrought forms.

7. The salt-water corrosion resistance of these alloy compositions is from 10 to 100 times greater than that of common magnesium alloys. Strength tests on some high-purity casting alloys show negligible loss in properties after 6 months' alternate immersion in 3 per cent NaCl.

APPENDIX A.—*Analysis Technique*

In the analysis two pairs of solid metal electrodes 11 by 3.5 mm. were cut from the specimen to be analyzed. The surfaces from which the discharge was to take place were polished on an Aloxite sanding wheel and carefully cleaned by allowing 3 N hydrochloric acid to flow over the area for 10 to 15 sec. The electrodes were then rinsed in distilled water and dried on a clean cloth. This cleaning treatment was given the electrodes immediately before they were placed in the electrode holder, in order to reduce chances of contamination to a minimum. The electrodes were placed in a water-cooled electrode holder with a gap of 5 mm. between the electrodes. In analyzing magnesium and its alloys for iron, nickel and lead at concentrations below 0.1 per cent and silicon at concentrations below 0.01 per cent, a 2.5-amp. d.c. arc source was used. The arc was struck with a pure graphite rod. No lens was used between the source and the spectrograph slit, the source being placed at a sufficient distance from the slit to make sure that all light that passed through the slit also passed through the spectrograph lens. The spectra were recorded on Eastman polychrome plates by means of a medium quartz spectrograph.

In the determinations a blackening-logarithm-of-intensity calibration pattern was placed on each plate in addition to the spectra of the specimens. Calibration was accomplished by photographing a continuous light source through a Hansen step-diaphragm according to the method of Thomson and Duffendack.² The blackenings (defined as the difference between the peak of the galvanometer deflection of a microphotometer for the spectral line and the deflection for the transparent plate) of the selected spectral lines and of the steps of the intensity calibration pattern were obtained by means of a nonrecording microphotometer. From the blackenings of the steps of this pattern, a characteristic

curve for each plate was drawn and was then used to determine the logarithm of the relative intensity of the selected line pair. This procedure, carried out for a series of specimens of known composition in which the element under analysis varied over the desired concentration range, yielded an analytical curve for the analysis of this element. The analysis of a specimen of unknown composition was made, applying the logarithms of the relative intensities of the selected spectral line pairs determined in the manner described above to the appropriate analytical curve and by reading therefrom the percentages of the elements under test.

In the analysis of magnesium for aluminum, calcium, copper, manganese, silicon, zinc and cadmium, lead and tin at concentrations greater than 0.1 per cent, the procedure used was similar to that outlined above except that a condensed spark source was used in place of the direct current arc.

The procuring of satisfactory standard specimens to be used in constructing the analytical curves referred to above offered no difficulty in the case of metal concentrations of 0.1 per cent or greater. The obtaining of satisfactory standards in the concentration range below 0.1 per cent did, however, present a real problem. All standard specimens used in the latter concentration range were made by adding known amounts of the various constituents to sublimed magnesium. These specimens were then carefully analyzed by the following chemical procedures:

The thiocyanate and the $\alpha\alpha'$ dipyridyl methods were both used to aid in the standardization of the iron analysis. The $\alpha\alpha'$ dipyridyl method was less critical to slight changes in the analytical technique and, since both methods gave the same result, it was the method used in the analysis of most of the standard samples.

At the beginning of this investigation no chemical method was developed that

would yield a satisfactory analysis for nickel in magnesium in the order of 0.001 per cent. There were satisfactory methods, however, for the analysis of nickel in the range 0.1 to 1.0 per cent concentration. To obtain the standard specimens, alloys with nickel contents of 0.1 to 1.0 per cent were first prepared. After satisfactory chemical analyses of these specimens were obtained, the specimens were diluted by known amounts with nickel-free magnesium. Since nickel is completely soluble in magnesium in this concentration range it was possible to prepare satisfactory standards in this manner covering the concentration range of 0.00025 to 0.05 per cent. A modified furil dixime method for this determination has since been developed. Results obtained by this chemical method and by the spectrochemical method based on the standards prepared in the manner described above are in very good agreement. The average error of the spectrochemical analysis in the range of 0.002 per cent iron and nickel based on triplicate determination is ± 0.0005 per cent.

The standard specimens for the analysis of lead in magnesium were analyzed by the colorimetric dithiazone method.

The chemical silicon determinations in concentrations below 0.05 per cent were made by the molybdate colorimetric procedure.

The electrolytic, colorimetric and iodide methods were used for the chemical determination of copper. The electrolytic method was most satisfactory at concentrations of the order of 0.1 per cent and higher. Below this figure the colorimetric and iodide methods were more sensitive and accurate.

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DISCUSSION

(P. T. Stroup presiding)

P. T. STROUP,* New Kensington, Pa.—This is a significant contribution in the field of corrosion studies of magnesium. I think it rather strikingly illustrates the extensive damage caused by new traces of iron and magnesium and the remarkable effect in counteracting this that is caused by manganese.

E. A. ANDERSON,† Palmerton, Pa.—This paper is so beautifully and comprehensively written as to be readily understandable without hard work, yet it encompasses a great deal of really good research.

The paper illustrates something that we do not all think about enough; that is, we do not really know the properties of an element. We are only beginning to grope nearer to that knowledge. We have been talking about magnesium as nonresistant to chloride, with all the qualifications these authors have put on that statement. Now we find that when we approach the elemental form it is an entirely different product.

Workers in industrial research laboratories ought to pay more attention to this basic problem of trying to produce a metal that is really pure, and try to find out what it really is.

L. W. KEMPF,‡ Cleveland, Ohio.—It would be interesting to know the actual concentra-

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tions of iron and perhaps copper and nickel in the specimens.

J. D. HANAWALT (author's reply).—I should like to further emphasize Mr. Anderson's comments about the importance of knowing the inherent characteristics of pure materials. Without knowing the drastic effects of trace impurities on corrosion resistance in aqueous media, one is likely to place magnesium in a class with calcium instead of in a class with aluminum, and, further, to assume that the solubility or the density or some other characteristics of its naturally forming film is responsible for its behavior and that nothing can be done about it. Actually, its protective film characteristics are quite adequate in the absence of cathode electrodes with large driving potentials with respect to magnesium, and the inherent characteristic of magnesium that is different from that of other corrosion-resistant metals is its high anodic solution potential. The problem then becomes one of contact corrosion.

In answer to Mr. Kempf's question on the composition of the specimens, the data for which are shown in Fig. 15, the concentrations of impurities in these specimens fall in the range of less than one thousandth iron, less than one hundredth copper, and less than one thousandth nickel.

Since the present paper was submitted for publication, an article by A. Beerwald has appeared in *Zeitschrift für Metallkunde* [(1941) 33, 28] which covers some of the same subject matter as the present paper and requires discussion, particularly in connection with the conclusions of the two papers. The title of the paper is "The Influence of Impurities on the Corrosion Behavior of Magnesium and Its Alloys with Manganese and Aluminum."

The paper presents the analysis of cell

magnesium and of distilled magnesium, notes the extreme difference in salt-water stability between them and concludes that the difference must be due to Fe or Cl. The specimens were prepared from the distilled magnesium as base, and the rate of hydrogen evolution during the first few days exposure to 3 per cent NaCl was measured. In agreement with the present authors, Beerwald found no detrimental effects due to Cl. However, because of the way in which his experiments were carried out, he states his conclusion on the effect of iron so that it sounds in absolute contradiction to ours, whereas in reality, the two papers are in complete agreement insofar as they are related. For this reason it seems desirable to discuss Beerwald's paper at this time. With respect to iron, Beerwald states in his conclusion that the corrosion rate is greatly increased by a trace in the order of thousandths per cent and increases with increasing iron content until the percentage of iron reaches about 0.03 and that higher percentages of iron over this amount are only of small significance. Beerwald's observations are limited to the early stages of coating formation and his conclusions, therefore, refer to the initial rates of corrosion, whereas our rates represent a steady-state condition.

Our hypothesis, that the initial period of corrosion is one in which cathodic impurities are being undermined and removed or are being covered over by spread of the anodic film, would predict results similar to those of Beerwald's; though with the additional condition that, if impurities are below the tolerance limit, a final steady state of low corrosion rate is reached after about eight days. These results are given more fully in a recent publication by R. E. McNulty and J. D. Hanawalt [Preprint 81-12, Electrochem. Soc. (April 1942)].

Recrystallization and Precipitation on Aging of Tin-bismuth Alloys

By J. E. BURKE,* AND C. W. MASON,† MEMBER A.I.M.E.

(Philadelphia Meeting, October 1941)

IN attempting to study precipitation from a tetragonal lattice, using solid solutions of bismuth in tin, it was found that although a Widmanstätten pattern is observed^{1,4} only a qualitative analysis of the orientation relationships is possible, because of the unusual structural changes that accompany the precipitation process.

MICROSCOPICAL STUDIES

Alloys were made from Chempur tin (Standard samples 42b and 42c, National Bureau of Standards), and bismuth (Kahlbaum C.P.) by melting weighed quantities together under palm oil, stirring well, and casting in a heated graphite mold.

The polishing and etching techniques employed largely govern the visibility of the structural changes.

The preliminary surfacing operations were similar to those recommended by Villela and Bergekoﬀ,⁵ through Behr-Manning 3/0 abrasive papers, lubricated by a solution of paraffin in kerosene. A rough metallographic polish was next given, using a thin cotton cloth charged with relevelated alumina (maximum particle size of about 4μ) and soap solution; repeated etching and polishing served to remove disturbed metal.

For high-power examination better preparation was necessary. It was found that on such soft metals the threads of the fabric, rather than the abrasive, cause most of the scratching. Cotton outing

flannel, which had been brushed so that the nap lay down, was fairly satisfactory, but a heavy grade of silk velvet (not the noncrushable kind) was found to be better, especially after some use.

A better procedure was as follows: The metal lap was warmed slightly, and a 4-in. circle of woolen broadcloth was cemented to its center by a thin film of melted paraffin. The broadcloth was then moistened with water, and a 30 to 40 per cent solution of sodium hydroxide heated to about 50°C. was poured over it, allowed to stand for 1 to 2 min. and then washed off. It was neither necessary nor desirable to remove all the sodium hydroxide from the cloth, since its etching action aided in the removal of the flowed layer from the sample. The cloth was then charged with a paste of the relevelated alumina in water.

Since this lap did not remove deep scratches, it was necessary previously to polish the specimen on some material such as the silk velvet. The sodium hydroxide softens and partly gelatinizes the woolen lap covering, permitting a scratch-free polish, but its action continues, and the cloth deteriorates after about 24 hr. This is not serious, because a new lap can be prepared in about 5 min., and only small pieces of cloth are used.

Etching with a strongly acid solution of ferric chloride was found satisfactory for removing the flowed layer. For the final etching, the most satisfactory reagent was that of Taffs,⁷ the formula for which is: $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 2 grams; HCl , 5 c.c.; H_2O , 30 c.c.; $\text{C}_2\text{H}_5\text{OH}$ (95 per cent), 60 c.c. This etchant reveals differences in com-

Manuscript received at the office of the Institute Dec. 10, 1940; revised May 2, 1941. Issued as T.P. 1364 in METALS TECHNOLOGY, September 1941.

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† Professor, Chemical Microscopy and Metallography, Cornell University, Ithaca, N. Y.

¹ References are at the end of the paper.

position and orientation in the tin-rich matrix, but does not attack the precipitate.

Changes on Aging

Metallographic examination of an as-cast 90-10 tin-bismuth alloy immediately after freezing shows that coring has been so extreme that in many places free eutectic bismuth is present. Such extreme coring, even with slow solidification, indicates a very low diffusion rate, because the solid solubility of bismuth in tin is more than 21 per cent at the eutectic temperature. Coring with respect to bismuth was observed by Mason and Forgeng⁶ in "pure" tins containing 0.001 per cent Bi.

After the 10 per cent Bi alloy has been aged at room temperature for about 2 hr., precipitation of a new phase commences at many points along the dark-etching lines of the cored structure; that is, in the regions of high bismuth content corresponding to the last portions of the dendrites to solidify. The patches of precipitate grow along these regions until they meet. Fig. 1 shows the appearance of such a specimen after aging at room temperature for three days. The precipitate has to some extent the geometrical arrangement characteristic of a Widmanstätten structure, but it is poorly formed and the lamellae are very fine (Fig. 2).

The precipitated phase is certainly bismuth; according to most of the constitutional diagrams bismuth is the only phase that would be expected to appear from the supersaturated solid solution. Furthermore, Solomon and Morris-Jones,² in their X-ray study of an alloy containing 50 per cent Bi and 50 per cent Sn (in which some 20 per cent of the bismuth would have been in solid solution, to yield a precipitate phase) found that all the observed powder lines could be explained either by the β -tin lattice or the bismuth lattice.

Precipitation proceeds more slowly in the low-bismuth central ribs of the dendrites,

but after a week or so it has advanced to these regions, giving more widely spaced lamellae of bismuth and a better formed Widmanstätten pattern there.

Precipitation is very slow in the alloys containing less bismuth, particularly if they have been homogenized at 1115°, to reduce coring. After several weeks, only a few bismuth particles could be found at the grain boundaries, in 5.5 and 8 per cent Bi alloys. A 5 per cent Bi alloy aged at room temperature for 5 years also showed only a small amount of precipitation.

Unprecipitated samples were aged at various temperatures up to 80°C., with little improvement in the Widmanstätten pattern. The rate of precipitation was less at the higher temperatures.

Recrystallization of Matrix on Aging

At the edge of the region where precipitation has occurred there is a sharp change in the etching characteristics, the matrix of the bismuth precipitate usually being much less darkened than the parent solid solution in which the precipitate patch was growing (Fig. 3); this change is due to depletion in bismuth content. Furthermore, when two patches that have commenced at different points in the same parent crystal grow until they meet, a grain boundary is visible between them, and the Widmanstätten arrangement in the two grains is different (Figs. 2 and 4). These facts indicate that some sort of recrystallization accompanies the precipitation; differences in color between various precipitate patches originating in the same parent grain (Fig. 1) confirm this interpretation.

The term "primary" will be applied to the homogeneous solid solution phase that forms directly from the melt, and the term "secondary" to the reoriented matrix, which grows in patches from the primary phase simultaneously with the precipitation of the bismuth.

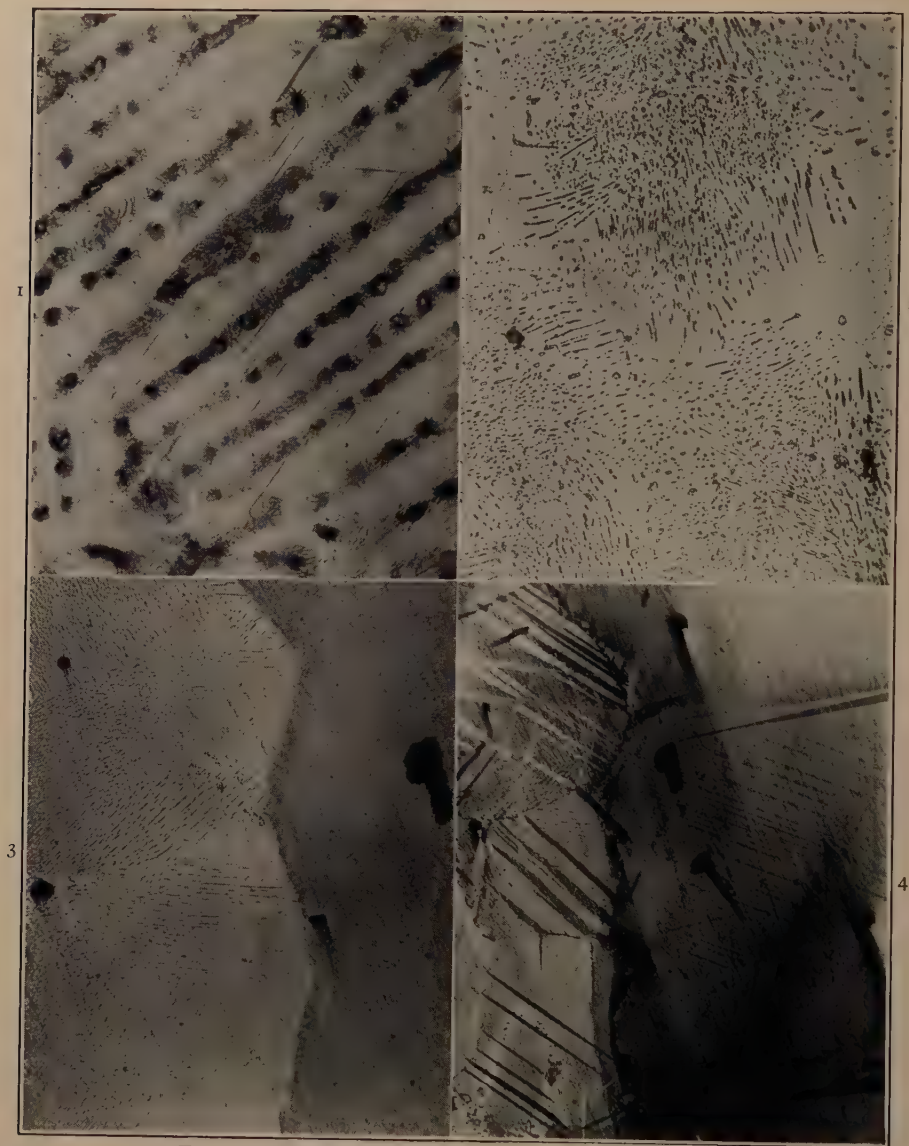


FIG. 1.—10 PER CENT BISMUTH, 90 PER CENT TIN. $\times 200$.
Recrystallization and precipitation occurring in patches along dendrites of cast single crystal, after aging 3 days at room temperature.

FIG. 2.—9 PER CENT BISMUTH, 91 PER CENT TIN. $\times 500$.
Grain boundaries and imperfect Widmanstätten pattern, in secondary grains of aged alloy.

FIG. 3.—9 PER CENT BISMUTH, 91 PER CENT TIN. $\times 200$.
Adjacent secondary grains, growing into matrix of primary solid solution.

FIG. 4.—SAME ALLOY AS FIG. 3, $\times 100$.
Area of Fig. 3 is included at upper left. Aged, and twinned by deformation, showing changes of direction in twin bands as they cross boundaries of secondary grains. Highly oblique illumination.

Behavior on Deformation

Further proof that a reorientation accompanies the precipitation was obtained by deforming a partly precipitated specimen to produce mechanical twin bands. Fig. 4 shows such a specimen. A grain boundary in the primary phase runs across the specimen just outside the left of the picture and the secondary growth is proceeding toward the right. The dark part on the right is the untransformed matrix, which has only one orientation, as shown by the twin bands, which are strictly parallel over its whole area. When one of the twin bands in the unprecipitated portion comes to the boundary of the precipitated region, it either stops or changes its direction, and the directions of the twin bands in different secondary crystals derived from the single parent grain are different. Since all the precipitate patches certainly twin with the same composition plane, this difference in adjacent grains that were strained similarly is proof that each secondary patch is differently oriented.

The progress of the precipitation also is shown in this photograph. The specimen had been polished, etched, and aged 4 days before it was deformed. The boundary between the precipitated and unprecipitated regions at the time of deformation is boldly shaded, owing to an "orange-peel" effect of distortion. To the left of this line can be seen the boundary line at the time of the original polishing, shown by the discontinuity in etching. Thus the three separate new grains are certainly growing into the unprecipitated matrix, which is a single crystal.

The difference in orientation of two of these grains can also be distinguished by the difference in their Widmanstätten patterns. This is shown in Fig. 3, which is the same field as the upper left-hand part of Fig. 4. The advance of the precipitate patch since the time of etching is less

apparent in this photograph, because the specimen had not yet been deformed.

The recrystallization that accompanies the precipitation of bismuth produces a very small secondary grain size. It was not found possible, by reducing concentrations, gradients, or degree of undercooling, to obtain secondary grains of adequate size for investigation of their orientation, and that of the precipitate within them. Specimens were cast in a split graphite mold, and aged to allow precipitation before any possible deformation from sectioning and polishing had occurred; these showed the recrystallization, which therefore cannot be due to mechanical strain introduced before or during preparation.

When mechanical strain was applied to the specimens before aging, many twin bands were produced. Upon aging at room temperature, the growing secondary patches consumed primary matrix and twin bands alike, as can be seen in Fig. 6, and no trace of the previously twinned structure could be found in the newly formed grains. If a Widmanstätten mechanism were controlling the orientation of the new grains, a band of different orientation should appear in the secondary grain, corresponding to the twin band in the primary grain. Evidently, if any Widmanstätten mechanism operates to control the orientation of the secondary grains, it does so only in nucleation, and subsequent advance of the front of the secondary grain into the primary grain occurs in the same way as simple grain growth.

This deformation does not appear to accelerate the precipitation process, but severe work, such as that produced by a deep scratch in the surface, caused a complete recrystallization of the matrix, accompanied by granular precipitation of the bismuth. Surface working from improper polishing may, after aging for several days, give rise to similar precipitation.



FIG. 5.—10 PER CENT BISMUTH, 90 PER CENT TIN. $\times 500$.
Detail of secondary grain, after mechanical twinning.

FIG. 6.—10 PER CENT BISMUTH, 90 PER CENT TIN. $\times 100$.
Secondary grain growing in twinned solid solution matrix.

FIG. 7.—10 PER CENT BISMUTH, 90 PER CENT TIN. $\times 100$. SAME FIELD AS FIGURE 6.
Thirty-minute solution heat-treatment at 115°C . Secondary grain being consumed by matrix,
with restoration of twin bands.

FIG. 8.—SAME AS FIG. 7., AFTER 15-HOUR SOLUTION HEAT-TREATMENT AT 115°C . $\times 100$.

Effect of Eutectic Bismuth

Although many of the patches in the 10 per cent Bi alloy have a particle of eutectic bismuth at their center, eutectic pattern or orientation does not control the orientation of the secondary phase. A 9 per cent Bi alloy was annealed for two months at 115°C.; this treatment redissolved almost all of the eutectic, and decreased the coring. Room-temperature aging for one day then caused precipitation to begin almost exclusively at the grain boundaries, with a variety of new orientations of the secondary patches.

When coring has been extreme enough to produce eutectic bismuth, the region around the particle of eutectic bismuth must contain the maximum possible amount of bismuth in solid solution (about 21 per cent at the eutectic temperature, while the room-temperature solubility is less than 1 per cent). Since the rate of precipitation increases greatly with supersaturation, it would be expected to begin first in these very unstable, highly supersaturated regions.

In annealed alloys in which the solid solution is homogeneous, or in alloys containing smaller amounts of bismuth in solid solution, the instability is not so great, and precipitation originates at the grain boundaries, in fewer places, so larger patches of precipitate are produced.

When an aged specimen is given a solution heat-treatment at 115°C., the precipitated bismuth dissolves in the secondary grains, and eventually these are "consumed" by the matrix from which they grew. All trace of the secondary structure may finally disappear, by a process of typical grain growth of the surrounding matrix at its expense.

A precipitate patch that has grown through adjacent twin bands in the matrix is similarly redissolved, the orientations of the twin bands, and their matrix supplant it by a process of grain growth (Figs. 6, 7, 8). Twinning mechanically produced in

the precipitate patch after aging apparently persists beyond the re-solution of bismuth, but recrystallization occurs as a result of the plastic deformation, and the process cannot be followed further.

X-RAY STUDIES

Experimental Procedure

Filings were taken with a jeweler's hack saw from a 9 per cent Bi alloy that had been annealed for 2 months at 115°C. These were passed through a 265-mesh sieve, made up into a very thin rod with Duco cement, and then annealed 24 hr. at 115°C., to redissolve any possible reprecipitated bismuth and remove the strain produced by the sawing operation.

For the high-temperature photograph, a small furnace was designed to be mounted directly on the goniometer head of the X-ray camera. It consisted of a square glass frame on which a resistance wire was wound, and a fine glass filament fused to the frame, to which the specimen was fastened with a dilute solution of Duco cement. The furnace was calibrated by slowly increasing the current passing through the radiant heating coil, until the melting of a very small piece of picric acid (m.p. 122°C.) on the glass filament was observed, by means of a microscope. The current thus determined was maintained during the exposure, for which copper K_{α} X-radiation was used.

Results

In order to determine whether the primary and secondary structures had the same lattice, three photographs were taken: one of a specimen at room temperature, immediately after the solution heat-treatment; one after aging 3 weeks at room temperature; and one at 115°C., above the range of precipitation. Some 18 lines of the tin lattice, in good agreement with the published data for interplanar distances, were identified in each

of these photographs, so it is certain that no phase change occurs on precipitation, and that tin is the parent phase from which the precipitation occurs, as well as the matrix of the bismuth in the precipitate patches.

There was no measurable difference between the spacings of the lines in pure tin and in the 9 per cent Bi alloy as cooled or at 120°C. This may be explained as being partly due to the small amount of bismuth in solution (5 atomic per cent), and partly to the similarity of atomic size, (the distance of closest approach of atoms in beta tin is 3.02 Å., and in bismuth is 3.1 Å.).¹¹

The room-temperature photograph of the fully aged specimen showed one line at 3.27 Å. corresponding to the strongest reflection from bismuth,⁹ which shows that precipitation had occurred to a considerable extent.

Three faint, broad, diffuse bands, corresponding to interplanar spacings of about 6.7 Å., 5.3 Å., and 4.05 Å., were observed in the aged alloy, and the unaged alloy showed a very faint line at about 4 Å.

These extra lines may possibly be explained as being due to a superlattice,¹⁰ which probably would not be very perfect in an alloy containing such a small amount of solute. Disordering might be expected to prevent their appearance in the photograph taken at 120°C.

DISCUSSION OF PRECIPITATION AND RECRYSTALLIZATION

The preceding data definitely show that the precipitation of bismuth is not due to a phase change in the matrix. Of the four types of precipitation from solid solution discussed by Mehl and Jetter,³ the foregoing observations correspond to the "discontinuous" type, which commences in small regions that spread in a wavelike manner, much as a polymorphic transformation would proceed; simultaneously with precipitation, the concentration of

the solute in the matrix changes abruptly from the original supersaturated value to the equilibrium value.

Apparently localized progressive recrystallization accompanying the precipitation, which is a distinctive feature of the Sn-Bi system,* has not previously been observed.

Recrystallization and growth of columnar crystals may occur when a constituent diffuses into or out of an alloy, as in decarburization of steel,¹⁴ but the greater part of these observations have been made on systems where the change in solute concentration causes a phase change. Rowland and Upthegrove¹⁴ also found that columnar crystals were formed when decarburization of steel occurred below the temperature of allotropic transformation. They consider lattice strains associated with concentration gradients as probable causes of the recrystallization.

Orientation Relationships

The presence of many directions of bismuth plates within a single secondary grain, and a different set of directions within each secondary grain, proves that the secondary matrix determines the orientation of the bismuth. If the bismuth lamellae determined the orientation of the matrix surrounding them, each parallel set of lamellae would have a different orientation of secondary matrix associated with them, which is not the case. We must therefore assume that the recrystallization precedes or at least occurs simultaneously with the precipitation of bismuth.

* Ageew, Hansen and Sachs¹² and later Barrett, Kaiser and Mehl¹³ did find that recrystallization of the matrix accompanied precipitation in the silver-rich alloys of silver and copper, and the latter authors showed that the new crystallites could be obtained from the parent one by a rotation of $42^\circ \pm 5^\circ$ about the axes [100] [010] [001]. This reorientation was detected only by X-ray means, and could not be observed microscopically because of the small grain size. No mention was made of any discontinuity in precipitation.

The fact that the growing secondary grains traverse twin boundaries in the primary grains without discontinuity shows that the primary matrix has no effect upon the orientation of the secondary patch after recrystallization has commenced. No parallelism was found between twin bands in neighboring secondary grains derived from a single primary grain, but since many orientations of secondary grains might ensue if a Widmanstätten mechanism were operating, and since for each secondary orientation several twinning directions are possible, the possibility of such a relationship cannot be excluded.

ATTEMPTS TO DETERMINE PLANE OF PRECIPITATION

The bismuth precipitate exhibits a Widmanstätten pattern, and direction frequency counts indicated that the bismuth lamellae occur in the plane of polish in at least six directions. If this number is accepted as correct, precipitation must occur along the crystallographic planes of at least two forms, since no single form in the tetragonal system would account for six directions. Because of the number of directions displayed, and the uncertainty in these directions, it is obvious that the plane of precipitation could not be determined without first knowing the orientation of the secondary grain. The back-reflection Laue method described by Greninger¹⁶ was tried but was unsuccessful. Satisfactory etching pits could not be developed, so that a method based on them could not be used.

The method that gave most promise was based on the directions taken by twin bands that could be developed by pressure in the secondary grains. Using the axial ratio of 0.5456, given by Mark and Polanyi²⁰ for tin, the composition plane for twinning is $\{301\}$.¹⁷ When the directions of twin bands on a single crystal of pure tin were plotted on a stereographic

projection according to the method outlined by Barrett,¹⁷ it was found that the orientation of the crystal could be determined with an accuracy of $\pm 1^\circ$, using traces in two surfaces. Incidentally, on this specimen, the traces of the dendrite branches could be seen; they were found to lie accurately parallel to $[110]$, which might be expected, since this is the direction of closest atomic spacing.

An aged 9 per cent Bi alloy was then twinned by pressure, polished and etched, and a large (2 mm.) grain which showed four twinning directions was selected and polished on two sides. Only one of the twin bands could be followed around the edge, but this fixed the position of one pole in a stereographic projection. The directions of the twin bands on both surfaces were plotted on a stereographic projection, and the pole corresponding to the twin band which had been followed around the edge was located, but an orientation could not be found where $\{301\}$ poles would simultaneously explain the position of the pole and the directions of the twin bands, so it was concluded that the composition plane for twinning was not $\{301\}$, as it is in pure tin. Several attempts were made to determine the composition plane, but difficulties caused by the small size of the grains to be dealt with, and the fact that usually only one well developed twinning direction would be shown in a grain, prevented its determination or its use to ascertain the orientation of the small grains.

Although the composition plane for twinning in the secondary grains does not appear to be $\{301\}$, in the unprecipitated alloy and in pure tin it is $\{301\}$. This was proved in the following manner: Using a pure tin single crystal as a seed, a long single crystal was obtained from the 8 per cent Bi alloy. A pure face was polished on it and twin bands were produced in the tin end, in the 8 per cent Bi end, and at the interface, by deformation

in a vise. The twin bands produced were parallel in all parts and several could be followed across the interface between the two compositions.

CONCLUSION

Without more knowledge of the orientations of the small secondary grains, within which the precipitate of bismuth occurs, any Widmanstätten relationship between them as matrix and the bismuth precipitate is not analyzable, beyond that based upon number of directions. The present study does offer an example of an apparently unique combination of "discontinuous" precipitation with simultaneous recrystallization. The following conclusions have been reached:

1. Room-temperature aging of tin alloys containing more than 5 per cent Bi gives rise to precipitation in patches, each of which increases in size by a process of grain growth irrespective of preexisting grain boundaries or twin bands in the parent solid solution.

2. X-ray diffraction studies show that, other than bismuth, no phase except beta tin is present in as-cast or precipitated specimens.

3. Within each secondary patch, the bismuth particles exhibit a Widmanstätten pattern and their matrix possesses a new orientation due to recrystallization accompanying the precipitation.

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DISCUSSION

(Edmund M. Wise presiding)

C. S. SMITH,* Waterbury, Conn.—I believe that eventually it will be found that recrystallization accompanies precipitation in many alloys, particularly those in which precipitation is of the microscopically discontinuous type. An interesting example is provided by beryllium-copper, in which the two types of precipitation are often observed simultaneously. The body of the grain precipitates normally with no change in microstructure, except for more rapid etching, until maximum hardness has been passed. The boundaries of the grains, even with short reheating periods, show areas of discontinuous precipitation that look not unlike nodules of pearlite in partially transformed steel. These areas cease to grow before they have spread far into the grains, however long the sample is annealed. An example of this microstructure is given by Mehl and Jetter in the American Society for Metals symposium report on Age-hardening of Metals, 1939, page 364. These dark-etching areas of discontinuous precipitation cannot be resolved under the microscope. If, however, the aged samples are subsequently annealed at a somewhat higher temperature—for example, 350°C.—for a suitable time, and then examined at a high magnification, it can be seen that the areas of discontinuous precipitation are composed of alpha completely recrystallized to an extremely fine grain size, mixed up with particles of the precipitated phase.

This behavior differs from that of the authors' bismuth alloy in that a large number of extremely small grains are formed, rather than a few big grains of an orientation different from the mother crystal.

In the beryllium-copper alloys there is a fairly large change of volume (contraction)

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associated with precipitation and it is probably the resulting strains that are responsible for recrystallization. Can the authors say how great is the volume change associated with precipitation in their tin-bismuth alloys?

D. W. SMITH,* New Kensington, Pa.—In the slide of Fig. 6, a patch of precipitated constituent was enclosed within a new recrystallized grain. One side of this recrystallized grain was straight and appeared to lie parallel or nearly so to the short twin bands within the parent grain. This would indicate a possible orientation relationship between the parent grain and the recrystallized grain. I wonder if the authors have made any effort to study possible orientation relationships existing between parent and recrystallized grains. If a rational relationship could be established, it would be of considerable fundamental interest.

J. E. BURKE (author's reply).—In reply to Dr. C. S. Smith, a volume change did result from the transformation. No quantitative measurements were made, but microscopically it appeared to be an expansion. This can be seen in Fig. 3, which shows a specimen that has continued to transform after etching. The new

front of the recrystallized grain can be seen just to the right of its former position, because of this volume change.

We found that in alloys containing smaller amounts of bismuth, say 3 or 4 per cent, precipitation occurred in an ordinary fashion, so that in these alloys, as well as in beryllium copper, two types of precipitation are observed.

In reply to Dr. D. W. Smith, we had hoped to be able to determine the orientation relationships, but we were unsuccessful. The grain size of the precipitated regions is very small and it is very difficult to determine the orientation of the secondary grains. It is possible that with the proper X-ray technique this could be done, and the orientation relationships established. An attempt was made to determine whether a parallelism existed between twin bands in various secondary patches originating in the same primary grain, but none was found. This, of course, does not mean that one does not exist. A form possessing a large number of equivalent planes might be involved, resulting in many orientations, so that a parallelism would not have been evident. The rectangular shape of the secondary patch shown in Fig. 6, with its side nearly parallel to the twin bands, was observed in several cases, but its significance was not determined.

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Electrochemical Behavior of the Lead-tin Couple in Carbonate Solutions

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(New York Meeting, February 1942)

THE high corrosion resistance possessed by tin under most circumstances, combined with its generally satisfactory appearance and useful physical properties,¹ has led to many and varied uses for the metal. These uses have been partly limited by the fact that tin is an expensive metal, therefore many applications have been developed in which tin has been employed in combination with lead, either by coating, as in tin-lined collapsible tubes, or by the formation of alloys containing various proportions of tin-rich and lead-rich phases, as terne plate. A detailed knowledge of the corrosion characteristics of the tin-lead couple therefore is of general interest and has become specially important at the present time, when every effort is being made to conserve tin as much as possible.

The present study has been limited to carbonate solutions with a pH range from 8.4 to 11.2 so that the results may be related to earlier work on the corrosion of tin and its alloys.^{1-3,6} In these papers, the effects of a number of anion and cation additions to these solutions have been observed.

APPARATUS AND METHOD

The electrodes for the corrosion cell were cut from rolled sheet about $\frac{1}{16}$ in. thick.

The length of all specimens was held constant at 7 in., while the width was varied from $\frac{1}{2}$ to 2 in. These electrodes were fastened to brass electrode supports, which were attached to rubber stoppers fitting into tall-type one-liter Pyrex beakers that contained the electrolyte. The lead electrodes were prepared from Omaha pig* and the tin was rolled from a slab of Chempur.† After cutting to size, the sheets were polished with No. 1 emery paper and cleaned with carbon tetrachloride. The edges, back and upper parts of the specimen were coated with a synthetic lacquer, which was supplemented with beeswax for the lead electrodes. The binding posts were coated with beeswax after the electrodes had been clamped. The pH of the electrolyte was controlled by adjusting the ratio of carbonate to bicarbonate. Approximately 600 ml. of electrolyte was used in each beaker. The entire assembly was placed in an oil bath thermostatically adjusted to operate at $30^{\circ}\text{C.} \pm 0.1^{\circ}$. Potentials were measured against a saturated calomel electrode connected to the cell by an agar-agar salt bridge. The carbonate solution used in the salt bridge was the same as that used in the corrosion cell. Currents were measured with a milliam-

Manuscript received at the office of the Institute Dec. 1, 1941. Issued as T.P. 1447 in METALS TECHNOLOGY, April 1942.

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¹ References are at the end of the paper.

* Typical analysis of Omaha pig: Pb, 99.98 per cent; As, 0.0000; Sb, 0.0002; Bi, 0.03; Zn, 0.0002; Cu, 0.0003; Ag, 0.0005; Fe, 0.002.

† Typical analysis of Chempur tin: Sn, 99.9919 per cent; Sb, 0.003; As, nil; Pb, 0.0027; Bi, 0.0006; Cu, 0.0005; Fe, 0.0013; Ag, nil; S, trace.

meter by the zero resistance method of Brown and Mears.⁴ The entire arrangement is shown schematically in Fig. 1.

In a typical run the lead samples were all coated so as to expose an area 2 in. wide

were run for lead by the same method used for tin¹ except that the vacuum anneal was omitted. The results obtained are plotted in Fig. 3. From these two figures it can be seen that the potential of tin is much higher

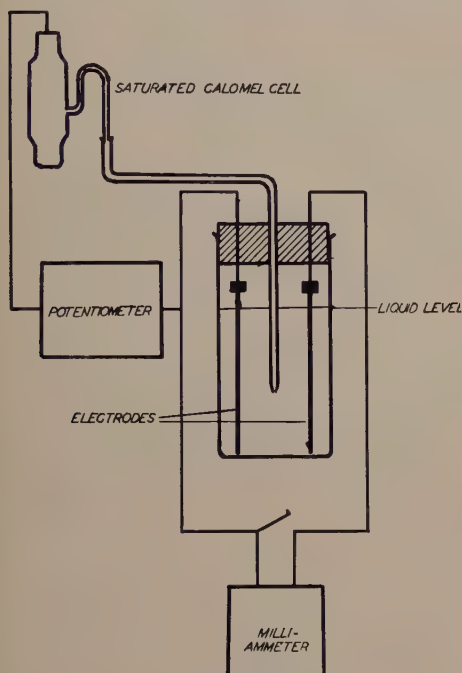


FIG. 1.—EXPERIMENTAL SETUP.

by 3 in. long; the width of the tin areas varied from $\frac{1}{2}$ in. to 2 by $\frac{1}{2}$ -in. increments. The beakers were all filled to a depth of 4 in. so that the exposed surfaces were totally immersed and the upper edge of the exposed area was about one inch below the surface of the electrolyte. The current and electrode potentials were measured periodically until they became reasonably constant.

In studying the lead-tin couple it is advantageous to know the potentials of the individual electrodes under the conditions of the test. The potentials* of tin are reproduced in Fig. 2. Potential-time curves

* Potentials are referred to a saturated calomel cell as zero, with noble metals like silver negative; i.e., increasing positive values indicate a greater tendency to corrode.

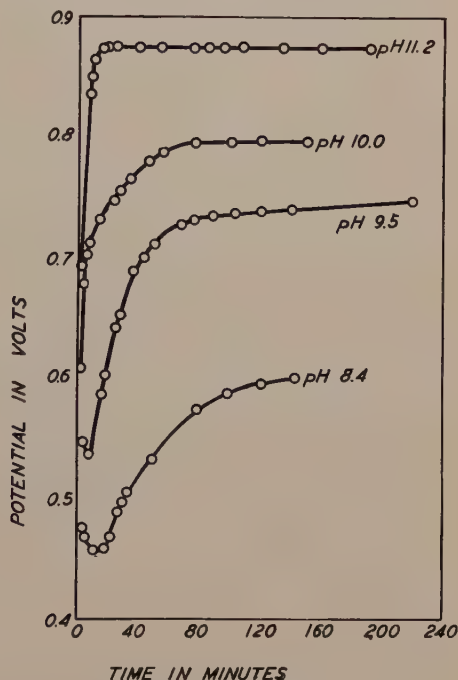


FIG. 2.—POTENTIAL TIME CURVES FOR TIN IN CARBONATE SOLUTIONS.

than that for lead, especially in the higher pH range. From this it can be deduced that tin should be anodic to lead. This has been found to be true in the higher pH range but at the lowest pH used, 8.4, lead is anodic to tin.

EXPERIMENTAL RESULTS

To establish the actual behavior of the cell, polarization curves for the lead-tin couple were determined. A current-time curve for a 2-in. tin 2-in. lead couple (since the length of all specimens was held constant at 3 in., only the width is used to designate the size of the electrode) in 0.1M Na_2CO_3 solution is plotted in Fig. 4. This curve is typical of all the curves obtained.

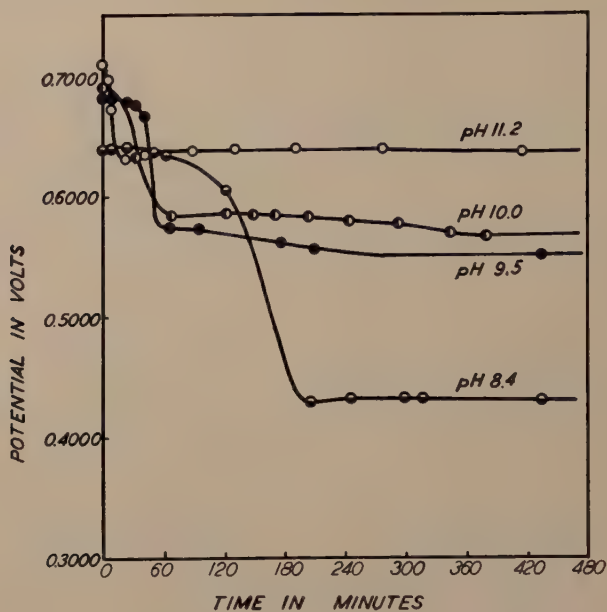


FIG. 3.—POTENTIAL TIME CURVES FOR LEAD IN CARBONATE SOLUTIONS.

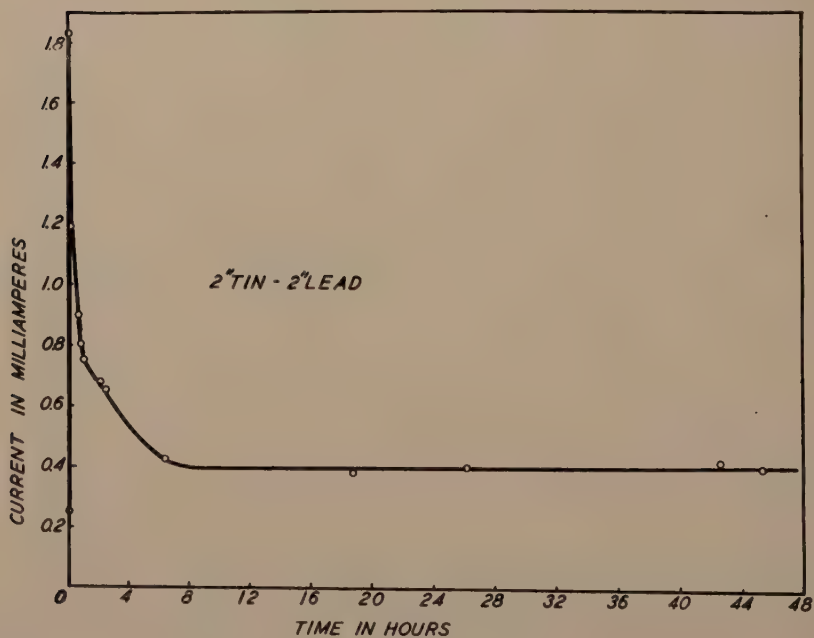


FIG. 4.—CURRENT TIME CURVES FOR 2-INCH TIN 2-INCH LEAD COUPLE.

The current goes up to a peak in the first few hours, then drops and remains virtually constant. This constant value of the current is reported as the equilibrium current

couples were run for 48 hr.; a few were run for five days but no appreciable change in the current or potential was noted. Both the current and potential varied during that

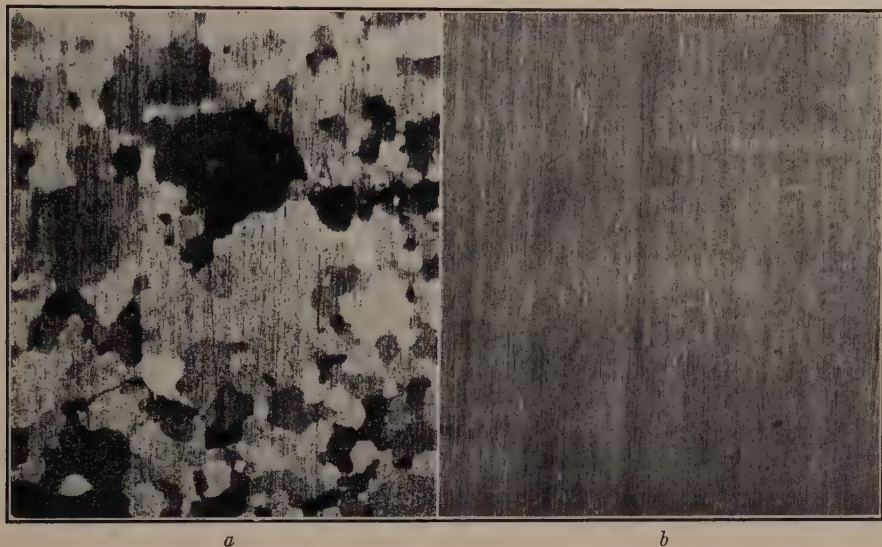


FIG. 5.—MACROPHOTOGRAPHS OF (a) TIN ANODE AND (b) LEAD CATHODE. $\times 6$.

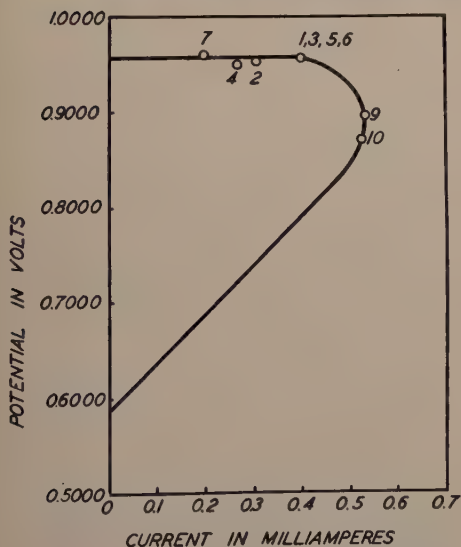


FIG. 6.—POTENTIAL CURRENT POLARIZATION CURVE FOR THE TIN-LEAD COUPLE IN 0.1M Na_2CO_3 .

for the couple in question. As the current approaches a constant value, the potential also becomes constant. The majority of the

period, but the average values were virtually the same as those obtained after 48 hours.

In the 0.1M Na_2CO_3 solution, the tin electrode is the anode and the lead electrode is the cathode. The tin specimens came out of the solution deeply etched and the lead specimens were the same as when the run started. Fig. 5 shows macrophotographs of a corroded tin anode and of a lead cathode after a run. These illustrate clearly the protective action of the tin.

The data obtained by varying the widths of the tin and lead electrodes independently with an electrolyte of pH 11.2 are given in Table 1. To illustrate the degree of reproducibility obtained, four independent runs are listed for the combination of a 2-in. lead electrode with a 2-in. tin electrode (Fig. 6). It is evident that when the tin areas are equal to or greater than the lead areas the cell is under cathode control; i.e., corrosion increases as the lead areas are increased but is small under conditions

encountered in practice when the exposed surface is essentially all tin. As the tin areas become smaller than the lead areas, some anodic polarization occurs, but the system remains under predominantly cathode control.

TABLE 1.—*Currents and Potentials for the Lead-tin Couple with Various Lead and Tin Electrode Widths in 0.1M Na₂CO₃ (pH = 11.2)*

Electrode No.	Size ^a	Potential, Volts	Current, Ma.	Calculated Weight Loss from Time Current Curves, Grams	Total Weight Loss of Tin Anode, Grams
1 1	2-in. Sn 2-in. Pb	0.957	0.40	0.0428	0.0751
3 3	2-in. Sn 2-in. Pb	0.960	0.39	0.0424	0.0767
5 5	2-in. Sn 2-in. Pb	0.959	0.41	0.0444	0.0741
6 6	2-in. Sn 2-in. Pb	0.957	0.40	0.0473	0.0748
7 7	2-in. Sn ½-in. Pb	0.961	0.20	0.0221	0.0708
4 4	2-in. Sn 1-in. Pb	0.948	0.27	0.0299	0.0708
2 2	2-in. Sn 1½-in. Pb	0.955	0.30	0.0337	0.0707
10 10	½-in. Sn 2-in. Pb	0.871	0.52	0.0662	0.0737
9 9	1-in. Sn 2-in. Pb	0.886	0.53	0.0596	0.0756
8 8	1½-in. Sn 2-in. Pb		0.52	0.0512	0.0751

^a The length of the electrode is held constant at 3 in., so only the width is reported.

At lower pH values the cell currents were too small to be read with any accuracy, and good polarization curves cannot be plotted. The data are recorded in Table 2, and the significant features are apparent. The tin areas remain anodic, and the couple remains under cathode control at pH values of 10.0 and 9.5. However, as the pH is reduced to 8.4, the lead areas become anode and the potential of the cell increases rapidly as the cathode areas are increased.

This means that under these conditions the couple is under anode control.

TABLE 2.—*Current and Potential Values for Lead-tin Couple in Carbonate Solutions*

Electrode Size, In.	pH of Electrolyte	Potential, Volts	Current, Ma.
2Sn-2Pb	10.0	0.616	0.08
1½Sn-2Pb	10.0	0.601	0.05
1Sn-2Pb	10.0	0.568	0.09
½Sn-2Pb	10.0	0.592	0.05
2Sn-2Pb	9.5	0.537	0.002
1½Sn-2Pb	9.5	0.556	0.002
1Sn-2Pb	9.5	0.534	0.002
½Sn-2Pb	9.5	0.557	0.001
2Sn-2Pb	8.4	0.499	0.06
1½Sn-2Pb	8.4	0.499	0.04
1Sn-2Pb	8.4	0.331	0.01
½Sn-2Pb	8.4	0.204	0.00

In order to determine the mechanism of the corrosion of the lead-tin couple, weight-loss measurements were made on some of the tin anodes. Then the electrochemical weight loss was calculated from the time-current curves. The calculated weight loss is always less than the total weight loss, therefore the actual corrosion is a combination of electrochemical and chemical corrosion. The values obtained from the electrochemical and total weight-loss experiments are reported in Table 1.

The influence of the following types of additions to the carbonate solutions of pH 11.2 has been determined: Cations, Ag⁺, Bi⁺⁺⁺, Ni⁺⁺, and Zn⁺⁺; anions, chromate, phosphate, and silicate; and agar-agar. Ag⁺, Cu⁺⁺, and Ni⁺⁺, and Zn⁺⁺ cations and silicate, chromate, and phosphate anions when added to sodium carbonate solutions tend to promote passivity of tin. In general, the following inhibitors are known to reduce the corrosion of lead: silicates, sulphates, carbonates, and colloidal substances.⁵ Since this present work is in carbonate solutions, the effect of the carbonate ion probably will mask the effect of other additions.

Since the carbonates of the cations listed above are only slightly soluble, of the order of 10⁻³ mols per liter or less, saturated

solutions of the cations listed above were used because the solubility of their carbonates is of the order of 10^{-3} mols per liter

TABLE 3.—Potentials and Currents for Lead-tin Couple with Inhibitor Additions

Addition to 0.1M Na ₂ CO ₃	Electrode Size, In.	Po- ten- tial, Volts	Current, Ma.
Ag ⁺	2Sn-2Pb	0.871	0.34
	2Sn-1½Pb	0.869	0.23
	2Sn-1Pb	0.869	0.15
	2Sn-½Pb	0.855	0.11
Cu ⁺⁺	2Sn-2Pb	0.864	0.40
	2Sn-1½Pb	0.863	0.31
	2Sn-1Pb	0.854	0.25
	2Sn-½Pb	0.862	0.16
Bi ⁺⁺⁺	2Sn-2Pb	0.957	0.21
	2Sn-1½Pb	0.947	0.29
	2Sn-1Pb	0.950	0.34
	2Sn-½Pb	0.910	0.37
	½Sn-2Pb	0.860	0.38
	1Sn-2Pb	0.916	0.32
	1½Sn-2Pb	0.841	0.42
	2Sn-2Pb	0.878	0.41
Ni ⁺⁺	2Sn-2Pb	0.957	0.12
	2Sn-1½Pb	0.953	0.19
	2Sn-1Pb	0.946	0.24
	2Sn-½Pb	0.947	0.32
	½Sn-2Pb	0.822	0.33
	1Sn-2Pb	0.852	0.32
	1½Sn-2Pb	0.849	0.33
	2Sn-2Pb	0.847	0.33
Zn ⁺⁺	2Sn-2Pb	0.860	0.36
	2Sn-1½Pb	0.677	0.28
	2Sn-1Pb	0.944	0.21
	2Sn-½Pb	0.867	0.18
	½Sn-2Pb	0.855	0.39
	1Sn-2Pb	0.872	0.37
	1½Sn-2Pb	0.905	0.30
	2Sn-2Pb	0.948	0.29
0.1 per cent agar agar	2Sn-2Pb	0.968	0.19
	2Sn-1½Pb	0.964	0.19
	2Sn-1Pb	0.965	0.14
	2Sn-½Pb	0.974	0.12
	½Sn-2Pb	0.859	0.28
	1Sn-2Pb	0.955	0.22
	1½Sn-2Pb	0.915	0.23
	2Sn-2Pb	0.964	0.23
0.01M Na ₃ PO ₄	2Sn-2Pb	1.005	0.12
	2Sn-1½Pb	1.003	0.14
	2Sn-1Pb	1.000	0.18
	2Sn-½Pb	0.995	0.21
	½Sn-2Pb	0.988	0.49
	1Sn-2Pb	0.973	0.45
	1½Sn-2Pb	0.990	0.27
	2Sn-2Pb	0.985	0.39
0.01M K ₂ Cr ₂ O ₇	2Sn-2Pb	0.585	0.02
	2Sn-1½Pb	0.587	0.02
	2Sn-1Pb	0.588	0.03
	2Sn-½Pb	0.568	0.04
	½Sn-2Pb	0.578	0.004
	1Sn-2Pb	0.571	0.02
	1½Sn-2Pb	0.579	0.02
	2Sn-2Pb	0.577	0.02
0.001M K ₂ Cr ₂ O ₇	2Sn-2Pb	0.618	0.02
	2Sn-1½Pb	0.618	0.02
	2Sn-1Pb	0.616	0.03
	2Sn-½Pb	0.607	0.04

TABLE 3.—(Continued)

Addition to 0.1M Na ₂ CO ₃	Electrode Size, In.	Po- ten- tial, Volts	Current, Ma.
1.0 per cent sodium silicate	2Sn-2Pb	0.600	0.05
	2Sn-1½Pb	0.597	0.03
	2Sn-1Pb	0.598	0.04
	2Sn-½Pb	0.590	0.03
	½Sn-2Pb	0.603	0.02
	1Sn-2Pb	0.587	0.03
	1½Sn-2Pb	0.591	0.05
	2Sn-2Pb	0.607	0.09
0.5 per cent sodium silicate	2Sn-2Pb	0.597	0.04
	2Sn-1½Pb	0.601	0.03
	2Sn-1Pb	0.598	0.03
	2Sn-½Pb	0.581	0.02
	½Sn-2Pb	0.593	0.01
	1Sn-2Pb	0.585	0.02
	1½Sn-2Pb	0.600	0.02
	2Sn-2Pb	0.600	0.04
0.1 per cent sodium silicate	2Sn-2Pb	0.588	0.28
	2Sn-1½Pb	0.579	0.26
	2Sn-1Pb	0.575	0.23
	2Sn-½Pb	0.557	0.12
	½Sn-2Pb	0.603	0.02
	1Sn-2Pb	0.587	0.03
	1½Sn-2Pb	0.591	0.05
	2Sn-2Pb	0.607	0.09

or less. They were saturated by adding excess reagent to the 0.1M Na₂CO₃ solutions several days before the experiment, shaking frequently and filtering just before use. The chemicals used were C.P. grade.

The results obtained with the various inhibitors are listed in Table 3. These additions can be divided into several groups according to their effect on the corrosion of the tin-lead couple. Ag⁺, Bi⁺⁺⁺, Cu⁺⁺, and Zn⁺⁺ have little or no effect on the corrosion behavior. Agar-agar and Ni⁺⁺ have almost no effect on the potential but they lower the current slightly. Trisodium phosphate increases the potential and lowers the current very slightly. Potassium chromate and sodium silicate lower the potential and current a great deal, but they also reverse the potential of the cell so that lead is anodic and tin is cathodic.

With all of the inhibitors used, the cell was under cathodic control; that is, a change in the anode area does not change the current, while a change in the cathode area changes the current. When potassium chromate or sodium silicate was used, the

lead was anode and the tin was cathode. Here any change in area of the tin changed the current, while with the other inhibitors the polarity was reversed, and any change in the lead area changed the current.

SUMMARY

1. In sodium carbonate solution with a pH 11.2 the tin-lead couple is under cathodic control and the anodic elements are tin.

2. In carbonate solutions with pH values of 10.0 and 9.5 the couple remains under cathodic control and tin remains anodic, but the corroding current becomes increasingly smaller.

3. In carbonate solutions with a pH of 8.4 the polarity of the cell has reversed so that lead is anode and the cell is under anodic control. The corroding current is very small.

4. In all of the above cases the corrosion is both chemical and electrochemical in character.

5. The effects produced by various additions to the carbonate solution with a pH of 11.2 are as follows:

a. Additions of Ag^+ , Bi^{+++} , Cu^{++} , Zn^{++} ions have no marked influence on the characteristics of the couple.

b. Additions of Ni^{++} and agar-agar reduce the current in the cell without altering the potential.

c. With all of the above additions the cell remains under cathode control.

d. Potassium chromate and sodium silicate reduce both the potential and the current considerably. However, they also reverse the polarity of the cell so that lead becomes anode.

6. Time-potential curves for lead in carbonate solutions with pH 8.4 to 11.2 have also been determined.

research program of which this investigation is a part. N. Y. A. assistants prepared many of the solutions and samples.

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DISCUSSION

(E. A. Anderson presiding)

E. A. ANDERSON,* Palmerton, Pa.—Two points about this paper seem to me very interesting. One point is the change of the anode potential with the pH shift of the electrolyte. The ordinary layman who first sees an electromotive series assumes that all sorts of galvanic corrosions take place and does not realize the shifts that are possible.

The other point is the interesting one that in couples the combination of electrochemical and chemical attack destroys the possibility of tying the whole thing up from the electrochemical viewpoint.

Dr. Wesley wrote a paper to prove that the electrochemical viewpoint holds. Perhaps he will comment on that.

W. A. WESLEY,† Bayonne, N. J.—The authors' observation that the calculated weight losses in Table 1 are always less than the corresponding total weight losses is the relationship generally observed in galvanic corrosion tests.⁷ It arises, of course, from the fact that some normal corrosion is taking place on the anode simultaneously with the galvanic corrosion. The results cannot be analyzed quantitatively in the absence of data on the

ACKNOWLEDGMENT

The Bristol-Myers Company, of New York City, and the Sun Tube Corporation, of Hillside, N. J., have sponsored the

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† Assistant Director, Research Laboratory, International Nickel Co.

⁷ W. A. Wesley: *Trans. Electrochem. Soc.* (1938) **78**, 539.

rate of corrosion of an uncoupled tin specimen under the conditions of test or data on the polarization curves for anodic and cathodic areas on a tin surface under the same corrosive conditions.

J. V. PETROCELLI,* Waterbury, Conn.—One of the principal conclusions drawn by the authors (No. 4 in the summary) is that the corrosion is both chemical and electrochemical in character. It would appear from the context that this conclusion is based on the data given in Table 1.

If the authors calculated their weight losses by the amount of current flowing from the tin to the lead specimens, as they seem to indicate, their conclusion is not necessarily valid. It is highly probable that there existed local corrosion cells on the anodic specimen (tin) itself so that the investigators were not tapping the total corrosion current.

An investigation in which the writer is at present concerned, on the electrochemical behavior of aluminum, zinc, and their alloys, indicates that it is quite possible for a corrosion current to exist between two metals A and B and yet have appreciable local corrosion currents on the more anodic electrode. It is hoped to have these data ready for publication at some future date.

MEMBER.—Could the inversion of anodic and cathodic behavior be expected to continue down into the neutral range and below as far as reagents are concerned? For example, when carbon dioxide is dissolved from the air in water solution, how would that affect the tin-lead couple?

G. DERGE (author's reply).—Dr. W. A. Wesley and Mr. J. V. Petrocelli point out the discrepancy between the calculated and measured anode weight losses. The authors recognize the fact that the measurement of the current between the tin anode and the lead cathode does not give the total corroding current on either tin or lead because of the local cells on the surface of each electrode. The difficulties inherent in determining the total corroding current on each anode and cathode area placed these measurements, desirable though they may be, beyond the scope and need of this research. By use of the term "chemical attack" the authors did not intend to preclude an electrochemical mechanism as the cause of the increased weight loss of the tin anode.

In answer to the last question, the authors can only say that the inversion takes place in the carbonate solution with a pH of 8.4. They have not tested the corrosion characteristics of the lead-tin couple in acid solutions. From these data, one could expect the lead to be anode to the tin in water containing dissolved carbon dioxide.

* Chemist, The Patent Button Co.

Internal Oxidation in Dilute Alloys of Silver and of Some White Metals

BY F. N. RHINES,* MEMBER, AND A. H. GROBE,† STUDENT ASSOCIATE A.I.M.E.

(New York Meeting, February 1942)

At elevated temperatures the oxide of silver is unstable in the air at atmospheric pressure, consequently no external oxide scale forms upon pure silver under conditions of high-temperature annealing. When small quantities of certain alloying elements are present in the silver, the formation of a thin external scale is possible¹ and in addition there may form a subscale composed of the oxide of the solute element precipitated within the body of the silver. Norbury² and Leroux and Raub³ have reported internal oxidation (subscale formation) in alloys of silver with 2, 7.5, and 30 per cent of copper. The presence of the subscale is believed to be responsible, at least in part, for the objectionable "fire mark" in Sterling silver.⁴ Several other alloys of silver, after oxidizing heat-treatments, are known to exhibit undesirable polishing characteristics that may be the result of internal oxidation. Except for the absence of an external scale of silver oxide, it is to be anticipated that silver alloys will prove to be very similar in their oxidation behavior to the alloys of copper, the oxidation characteristics of which have been studied in some detail.^{5,6} The present research confirms this anticipation. The oxidation of a series of 20 dilute alloys of

silver has been studied metallographically; some types of subscale not encountered among the copper alloys have been found.

Instances of internal oxidation in alloys of most of the metals of the I-b and VIII groups of the periodic system are on record, but evidence of this type of oxidation in alloys of the metals of the intermediate groups is lacking. A number of the metals of the intermediate group, among them cadmium, lead, tin, and zinc, appear to provide the conditions essential to subscale formation; i.e., they form oxides with a relatively low negative free energy of formation, they dissolve other metals that form more stable oxides, and, presumably, oxygen will diffuse through them. In a study of 40 alloys of these white metals only a few cases of internal oxidation have been found. The probable reasons for this difference in behavior will be discussed presently.

EXPERIMENTAL PROCEDURE

Silver.—The silver alloys employed in the oxidation studies were prepared in heats of 30 grams each from high-purity silver (99.993 per cent Ag)* and the purest avail-

Manuscript received at the office of the Institute Dec. 1, 1941. Issued as T.P. 1439 in METALS TECHNOLOGY, April 1942.

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¹ References are at the end of the paper.

* Producer's analysis of the silver: Ag, 99.993 per cent; Au, 0.0010; Cu, 0.0017; Fe, 0.0004; Pb, 0.0003; Bi, nil; Se, nil, Te, nil; Sn, 0.0010; Ni, tr.; Mn, tr.; Mg, tr. Analysis after melting and freezing in the manner followed in making the alloys: Ag, 99.98 per cent; Cu, 0.003; Pb, 0.001; Sn, 0.0003; Fe, 0.001.

It has been pointed out by the analyst that the larger quantities of impurities indicated in

able grades of the alloying elements, melted in new "electrode graphite" crucibles under a cover of borax. Instead of being cast, the melts were frozen in the crucibles, a rapid chill being obtained by quenching the crucible in water. Prior to oxidation the ingots were reduced 10 per cent by cold-forging, and the surface metal was removed, first by filing and then by grinding on 000 emery paper. A list of the alloys made is given in Table 1; the chemical analyses* were made on 1-gram samples taken in such a way as to be representative of all parts of the ingot.

of the oxidation characteristics of silver alloys at a single temperature and time. A temperature of 850°C. has been selected as the highest practicable for all of the alloys. The samples were set on edge on Sil-O-Cel bricks and were heated in a partly open electric muffle furnace controlled to a maximum temperature variation of $\pm 3^\circ\text{C}$. Except for alloys 29, 30, 31 and 32, which were heated for only $\frac{1}{2}$ hr., all alloys were heated for 3 hr. and were then cooled in the open.

Polished and etched cross sections of the samples were studied metallographically;

TABLE 1.—*List of Silver-base Alloys*

Alloy No.	Composition, Weight Per Cent, Balance Silver	Source of Alloying Element	Oxidation Behavior	Depth of Subscale after 3 Hr. in Air at 850°C., Cm.
3	0.41 Al	Hoopes aluminum	Subscale forms	0.0519
4	1.10 Cu	OFHC copper	Subscale forms	0.0945
7	2.79 Sb	Technical antimony	Subscale forms	0.0235
8	5.44 Zn	Horsehead Special	Subscale forms	0.0154
10	2.89 Sn	Straits tin	Subscale forms	0.0294
12	0.74 Bi	Technical bismuth	Subscale forms	0.1110
13	0.65 Pb	Omaha pig lead	Subscale forms	0.1108
14	0.26 Si	Technical silicon	Subscale forms	0.0100
15	2.48 Cd	Technical cadmium	Subscale forms	0.0276
16	Trace Cr	Technical chromium	Results uncertain ^a	
17	2.04 Mn	Electrolytic manganese	Subscale forms	0.0273
18	0.26 Zr	Technical zirconium	Results uncertain ^a	
19	1.36 Tl	Technical thallium	Subscale forms	0.1268
20	0.47 Ge	Technical germanium	Subscale forms	0.0551
21	0.40 Ni	Electrolytic nickel	β phase oxidizes	
22	0.73 In	Electrolytic indium	Subscale forms	0.0809
23	1.99 Mg	Distilled magnesium	Subscale forms	0.0167
24	Trace Ti	Technical titanium	Results uncertain ^a	
25	0.60 As	Black metallic arsenic	Subscale forms	0.0440
26	0.02 Fe	Carbonyl iron	Results uncertain ^a	
28	99.98 Ag	Pure silver	See text	
29	0.04 Fe	Carbonyl iron	Subscale forms	0.1000 ^b
30	0.04 Ti	Technical titanium	Subscale forms	0.1530 ^b
31	0.03 Zr	Technical zirconium	Subscale forms	0.0880 ^b
32	0.05 Cr	Technical chromium	Results uncertain ^a	

^a It is believed that the alloying elements were oxidized during melting.

^b Heated $\frac{1}{2}$ hr. at 850°C. in air.

Inasmuch as the nature and rates of internal oxidation have been studied in some detail for the copper-base alloys, it has been thought unnecessary to extend the present survey beyond an examination

the second analysis should not be taken to indicate that impurities have been introduced during melting because the precision of the second analysis is not as great as that of the first.

* Chemical analyses of the alloys were kindly made by the Handy and Harman Co., of Bridgeport, Connecticut.

the mode of oxidation observed and the depth of the subscale, where measurable, are reported in Table 1. Although many etches were tried, only one, composed of chromic and sulphuric acids and water,² was found to be generally satisfactory. Photomicrographs of the structures of the subscales are presented in Figs. 2 to 7.

White Metals.—Alloys of cadmium, lead, tin, and zinc (Table 2) were made from Omaha pig lead, Chempur tin, stick cadmium, Horsehead zinc, and the purest

available grades of alloying elements (same as listed in Table 1). Clay-graphite crucibles were used for melting and a charcoal cover for protection against oxidation. All



FIG. 1.—PURE CAST SILVER HEATED 3 HOURS AT 850°C. IN AIR. $\times 75$.

Shows fine grain size and grain-boundary ruptures near outer surface.

heats were cast in iron-chill molds, were scalped and, except for the zinc alloys, were reduced 66 per cent in cold-rolling. Prior to oxidation, the surfaces of samples cut from this material were ground on 000 emery paper.

In order to promote the most rapid oxidation in all of these low-melting alloys, heat-treating temperatures just below the solidus temperatures were chosen (Table 2). Longer times of oxidation were employed where very low temperatures of oxidation were required. A thermostatically controlled electric drying oven was employed for the oxidizing treatments.

The metallographic examination was carried out in the usual way. For etching the lead alloys, a solution composed of 80 per cent acetic acid and 20 per cent of a 3

per cent solution of hydrogen peroxide in water was used; for the tin alloys 5 parts of glycerin, 3 parts of acetic acid, and 1 part of nitric acid; for the cadmium and zinc alloys, an etch composed of chromic acid, a crystal of sodium sulphate and water was used. The results of these studies are

TABLE 2.—List of White-metal Alloys

Solvent Metal and Weight Per Cent of Solute	Temperature of Oxidation, Deg. C.	Time of Oxidation, Days	Oxidation Behavior
Sn + 0.05 Al	217	7	Intergranular oxidation
Sn + 0.1 Li	217	30	Li depletion zone
Sn + 0.01 As	217	18	External only
Sn + 0.01 Ba	217	18	External only
Sn + 1.0 Bi	217	18	External only
Sn + 1.0 Cd	217	18	External only
Sn + 0.01 Co	217	18	External only
Sn + 0.01 Fe	217	18	External only
Sn + 0.01 Ni	217	18	External only
Sn + 0.5 Sb	217	18	External only
Sn + 0.1 Zn	217	18	External only
Sn + 0.05 Mg	195	24	Intergranular oxidation
Sn + 0.05 Na	195	24	Na depletion zone and intergranular oxidation
Sn + 0.5 Pb	195	24	External only
Sn + 0.1 Ti	195	24	External only
Sn + 0.5 In	138	27	External only
Zn + 0.1 Mg	350	27	External only
Zn + 0.1 Cd	350	27	External only
Zn + 0.01 As	350	27	External only
Zn + 0.1 Sb	350	27	External only
Zn + 0.1 Bi	240	29	External only
Cd + 0.1 Bi	138	27	External only
Cd + 1.0 Mg	295	27	External only
Cd + 0.1 Zn	295	27	External only
Cd + 0.1 Ti	195	24	External only
Cd + 0.1 Pb	240	29	External only
Cd + 0.5 Sn	240	29	External only
Cd + 0.1 Sb	247	1	External only
Cd + 1.0 Li	295	30	External only
Pb + 0.05 Ca	295	27	External only
Pb + 0.5 Cd	295	27	External only
Pb + 0.5 In	295	27	External only
Pb + 0.1 Na	295	27	Subscale forms
Pb + 1.0 Sn	295	27	External only
Pb + 1.0 Ti	295	27	External only
Pb + 0.1 Zn	295	27	External only
Pb + 1.0 Bi	240	29	External only
Pb + 0.05 As	240	29	External only
Pb + 0.05 Li	217	28	Li depleted zone
Pb + 0.5 Sb	295	30	External only
Pb + 0.1 Mg	295	30	External only

summarized in Table 2 and the few instances of internal oxidation found are illustrated in Figs. 8 and 9.

DISCUSSION OF RESULTS

The pure silver employed in this research was found to be subject, during an oxidizing anneal, to a structural change in the surface



FIG. 2.—STRUCTURES OF SUBSCALES.

Upper four are arranged with outside surface of sample at bottom and unoxidized alloy at top. Arrows indicate limit of internal oxidation.

Lower four show oxide precipitate in each subscale. $\times 500$.

Al—Alloy No. 3, 0.41 per cent Al, balance Ag, heated 3 hr. in air at 850°C . Upper, $\times 75$.

Mg—Alloy No. 23, 1.99 per cent Mg, balance Ag, heated 3 hr. in air at 850°C . Upper, $\times 75$.

Ti—Alloy No. 30, 0.04 per cent Ti, balance Ag, heated $\frac{1}{2}$ hr. in air at 850°C . Upper, $\times 50$.

Fe—Alloy No. 29, 0.04 per cent Fe, balance Ag, heated $\frac{1}{2}$ hr. in air at 850°C . Upper, $\times 50$.

zone which caused a fine grain size and occasional disruption of the grain boundaries (Fig. 1). Probably this is not the result of the oxidation of a metallic impurity, for the effect appears in many of the alloys as well, and at the same time it never occurs to any extensive depth even though the oxidation of the alloying element may have penetrated far. No explanation of the effect is available. Undoubtedly this condition has some, though possibly small, influence upon the rates of internal oxidation of the alloys. It does not seem to have otherwise interfered with normal internal oxidation in the alloys of silver.

The structures of the subscales presented in Figs. 2 to 5 bear a striking resemblance to those previously found among the copper-base alloys.⁵ There is a wide variation in the particle size of the oxide precipitates, ranging from the microscopically unresolvable* in the alloys containing aluminum, titanium, iron and manganese to plates or needles 0.01 mm. long in the silver-copper alloy. The photomicrographs have been arranged with the alloying elements approximately in the order of descending negative free energy of formation of the oxides. With one or two exceptions, the particle sizes of the oxides are thus placed in ascending order. The most striking exceptions—magnesium, silicon and zinc—appear to be instances of segregation of the oxide in the silver grains rather than of an unexpectedly large individual particle size.

Widmanstätten precipitation of the oxides is again found among the silver alloys; notice in particular the alloys containing indium, tin, cadmium and copper. This type of structure is to be expected in all cases,⁵ but will not be obvious where the

particle size is very small or where it may be destroyed by liquation, as in the alloys of lead, tellurium, bismuth, silicon and arsenic, all of which form low-melting oxides. The appearance of the oxides in the latter group of alloys suggests that all were molten at the oxidizing temperature, as indeed they should be.

Among the silver-base alloys, as among the copper-base alloys, the inner limit of the subscale is nearly straight and parallel to the external surface of the sample wherever the oxides precipitate as discrete particles of uniform distribution throughout the grain. This has been taken to indicate that there is no significant anisotropy of diffusion of any of the elements taking part in the reaction.⁵ Where relatively large quantities of the alloying elements are present there is a marked tendency for the oxide to precipitate heavily at the grain boundaries and sometimes in a network (perhaps dendrite boundaries) within the grain. Dense precipitation of this kind appears to retard the passage of oxygen, for the growth of the subscale seems temporarily to be stopped in localities where the grain-boundary precipitation is heaviest, with the result that the inner limit of the subscale becomes irregular. Instances of this behavior are to be seen in the alloys containing magnesium, silicon, zinc and tin (Fig. 6).

A new type of internal oxidation was observed in the silver-nickel alloy containing 0.4 per cent Ni. The solid solubility of nickel in silver is extremely small, and the nickel appeared in the alloy chiefly as a second phase, β . No precipitation of nickel oxide within the silver grains was found; instead, the β phase oxidized progressively by subscale formation (Fig. 7). As might be expected, the oxidation of the β particles was not completed quickly except where they were very small. The larger β particles in the subscale zone are seen to be enveloped by a layer of oxide (Fig. 7), which appears to grow in thickness with passage

* Although the oxides could not be resolved at a magnification of 500 diameters, their presence was clearly indicated at low magnification by the zone of different etching characteristics near the surface of the samples (Fig. 2).



FIG. 3.—CROSS SECTIONS OF SUBSCALE IN FOUR ALLOYS. UPPER, $\times 75$; LOWER, $\times 500$.
 Arrangement described under Fig. 2.
 Mn—Alloy No. 17, 2.04 per cent Mn, balance Ag.
 Si—Alloy No. 14, 0.26 per cent Si, balance Ag.
 Ge—Alloy No. 20, 0.47 per cent Ge, balance Ag.
 In—Alloy No. 22, 0.73 per cent In, balance Ag.
 All heated 3 hours in air at 850°C .

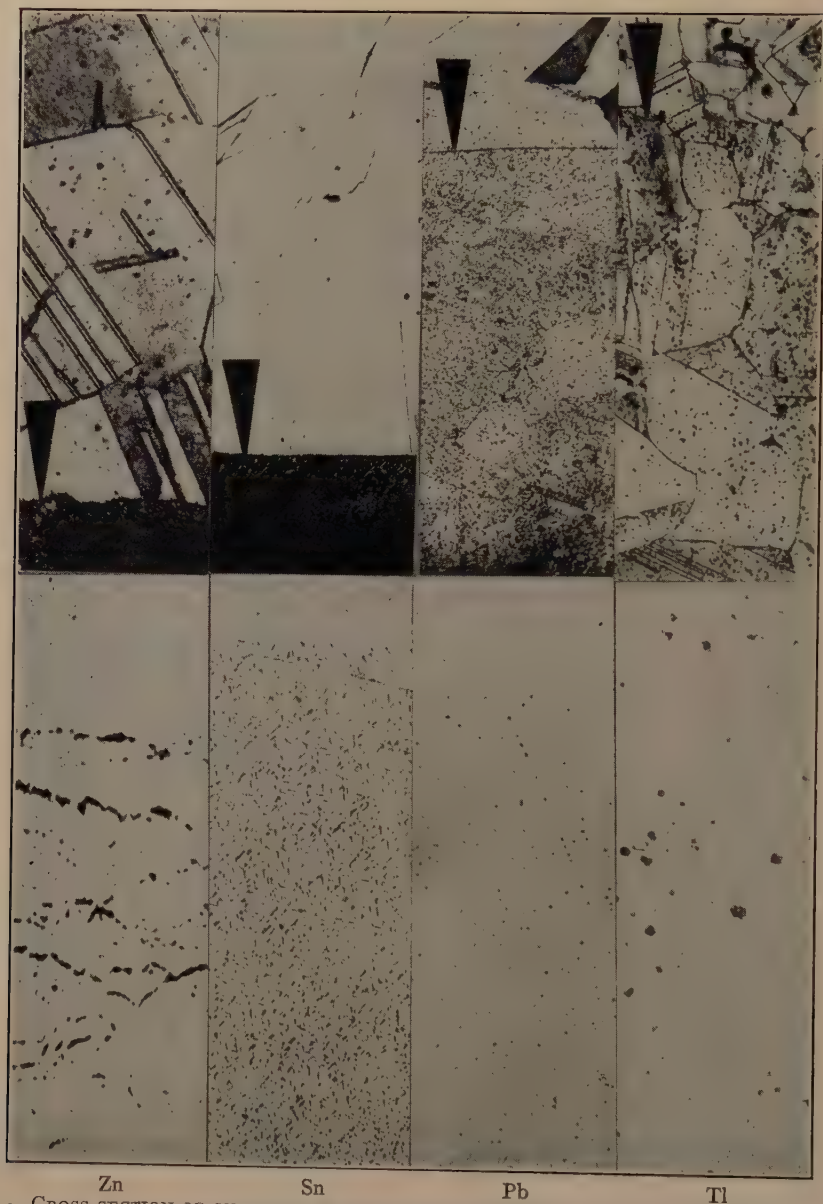


FIG. 4.—CROSS SECTION OF SUBSCALE IN FOUR ALLOYS. UPPER, $\times 75$ EXCEPT AS NOTED; LOWER, $\times 500$.

Arrangement described under Fig. 2.

Zn—Alloy No. 8, 5.44 per cent Zn, balance Ag.

Sn—Alloy No. 10, 2.89 per cent Sn, balance Ag.

Pb—Alloy No. 13, 0.65 per cent Pb, balance Ag. Upper, $\times 50$

Tl—Alloy No. 19, 1.36 per cent Tl, balance Ag.

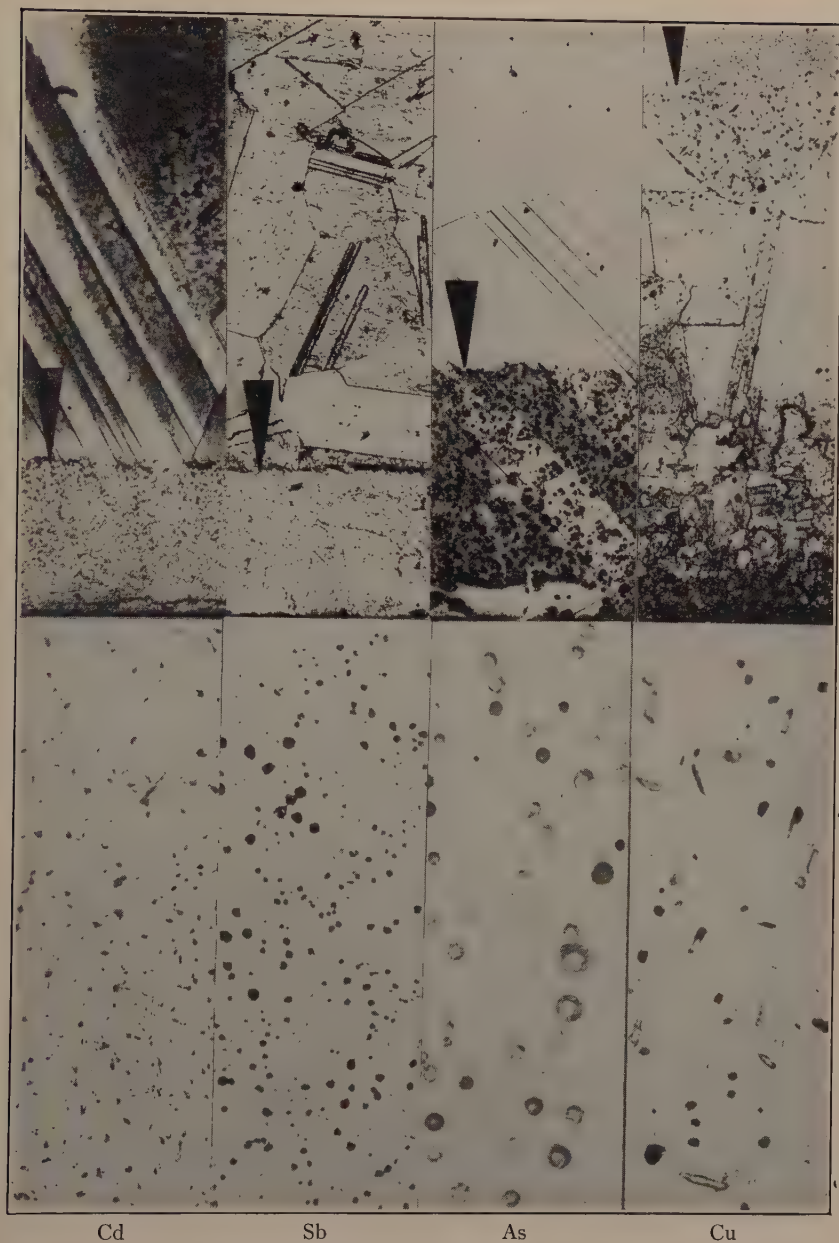


FIG. 5.—CROSS SECTION OF SUBSCALE IN FOUR ALLOYS. UPPER, $\times 75$; LOWER, $\times 500$.

Arrangement described under Fig. 2.

Cd—Alloy No. 15, 2.48 per cent Cd, balance Ag.

Sb—Alloy No. 7, 2.79 per cent Sb, balance Ag.

As—Alloy No. 25, 0.60 per cent As, balance Ag.

Cu—Alloy No. 4, 1.10 per cent Cu, balance Ag.

All heated 3 hours in air at 850°C .

of time until the β particle ultimately disappears.

No definite example of internal oxidation

tin with aluminum and with magnesium (Fig. 9) exhibited a kind of internal oxidation consisting in the precipitation of oxide

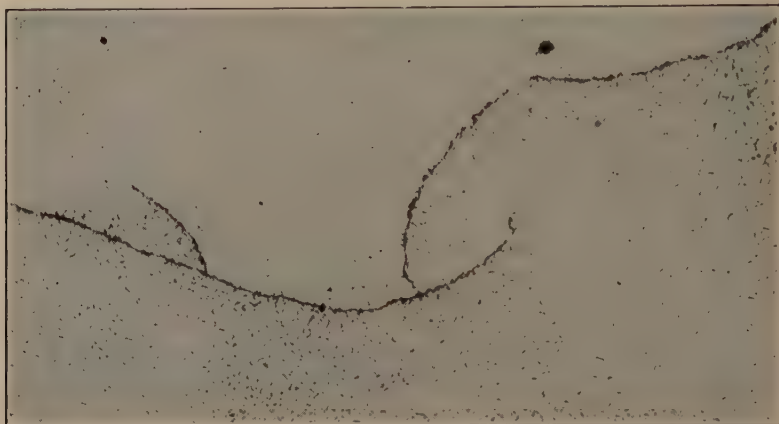


FIG. 6.—SILVER-TIN ALLOY NO. 10, OXIDIZED 3 HOURS AT 850°C. $\times 500$.

Same sample shown in Fig. 4, showing zone where barrier of heavy oxide precipitation has hindered normal subscale growth.

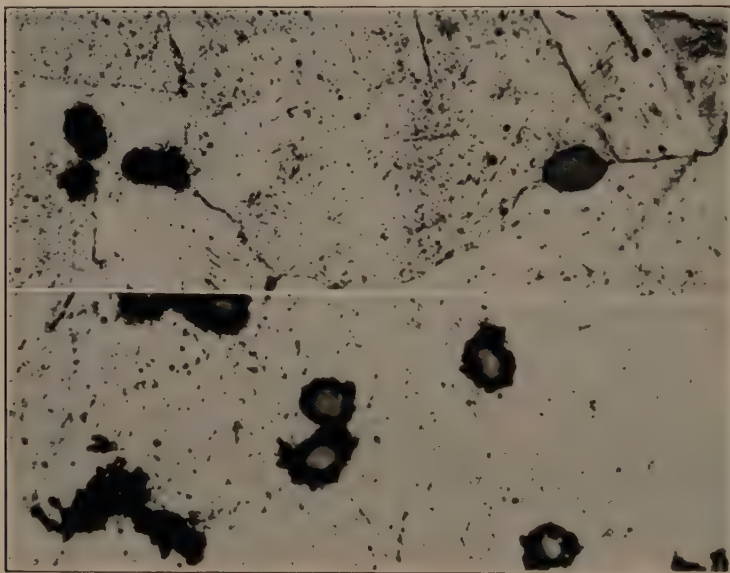


FIG. 7.—SILVER-NICKEL ALLOY NO. 21, OXIDIZED 3 HOURS AT 850°C. $\times 1500$.

Upper part shows condition at limit of oxidation. β particles at left are oxidized while β particle at right is unattacked. Lower part shows envelopment of larger β particles in oxidized zone.

was found among the zinc-base and cadmium-base alloys. An alloy of lead and sodium produced a normal subscale (Fig. 8), and alloys of lead with lithium and of

at the grain boundaries and, in the tin-aluminum alloy, along certain definite crystallographic directions as well. Otherwise oxidation among the alloys of lead,

tin, zinc and cadmium appeared to occur exclusively at the external surface. This does not necessarily mean that the internal structure of these alloys remained un-

these metals may be too low to permit internal oxidation. For internal oxidation to proceed within a reasonably short time, it is probably necessary for the rate of

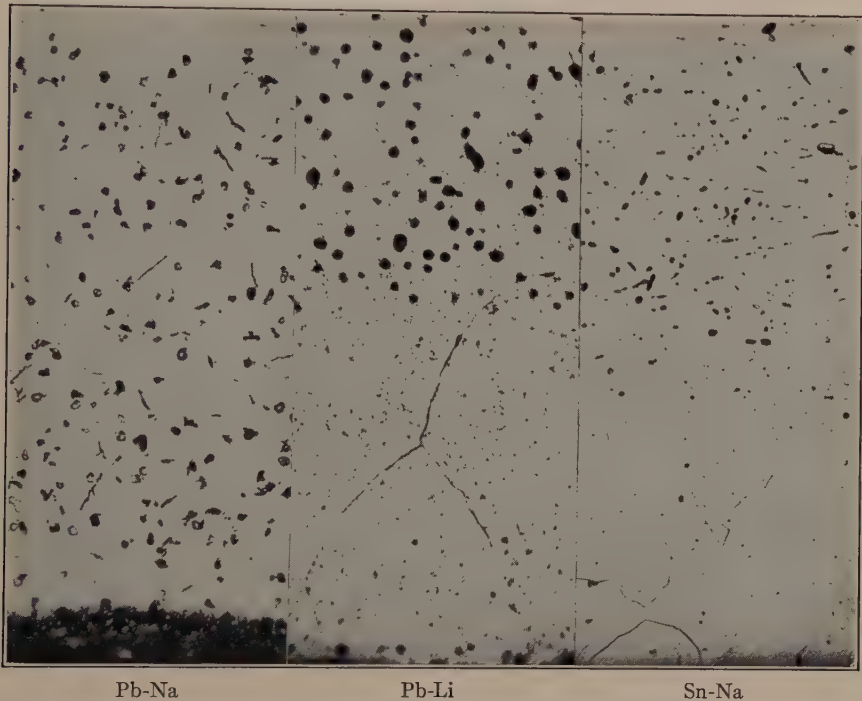


FIG. 8.—WHITE-METAL ALLOYS.

Pb and 0.1 per cent Na, oxidized 27 days at 295°C., shows true subscale, $\times 500$.

Pb and 0.5 per cent Li, oxidized 28 days at 217°C., shows zone from which Li has disappeared and grain-boundary oxidation, $\times 150$.

Sn and 0.05 per cent Na, oxidized 24 days at 195°C., shows zone from which Na has disappeared, no internal oxidation, $\times 150$.

altered; indeed, in many cases there was evidence of depletion of the alloying element near the surface of the metal. This is clearly shown by the elimination of the second phase in a zone near the surface in alloys of lead with lithium and of tin with sodium (Fig. 8).

The nearly complete absence of cases of internal oxidation among the alloys of the white metals probably is to be ascribed to an unfavorable relationship between the rates of diffusion of oxygen and the alloying elements in these metals. It is possible also that the solubility of oxygen in some of

diffusion of oxygen to be considerably greater than the rate of diffusion of the oxidizing substance; otherwise, the oxidizing element would be expected to diffuse to the external surfaces, there to oxidize under conditions more favorable to the nucleation of the oxide crystals. When the alloying element has been thus removed from a sufficiently wide zone its rate of delivery to the surface will have decreased to such an extent that oxygen may enter the metallic layer and precipitate a subscale. This state of affairs may not be attained for a considerable length of time,

however, so that internal oxidation may not appear within the time of a normal heat-treatment. A similar condition was observed in the internal oxidation of copper-

3. Tin diffusion through lead at 285°C . is $D = 1.6 \times 10^{-10}$ sq. cm. per sec.

4. Tin diffusion through silver at 285°C . is $D = 1.8 \times 10^{-13}$ sq. cm. per sec.

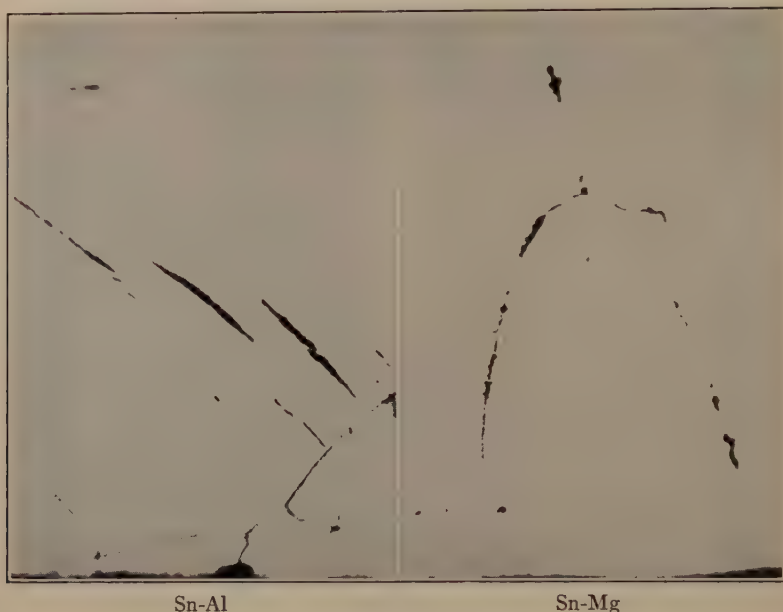


FIG. 9.—TIN ALLOYS.

Sn and 0.05 per cent Al, oxidized 7 days at 217°C ., shows oxidation at grain boundaries and along certain crystallographic directions, $\times 500$.

Sn and 0.05 per cent Mg, oxidized 24 days at 195°C ., shows grain-boundary oxidation, $\times 150$.

base alloys⁵; a narrow band containing neither oxide nor the alloying element was usually found next to the external surface.

Insufficient data are at hand directly to compare the rates of diffusion of oxygen and the metallic elements in the white-metal alloys that do not form subscales with those in copper or silver alloys that do form subscales. However, a general indication that the conditions postulated above are reasonable may be obtained from the following figures:

1. Oxygen diffusion through tin at 217°C . is 8.08×10^{-9} c.c. per sq. cm. per mm. per sec.*

2. Oxygen diffusion through silver at 217°C . is 1.53×10^{-10} c.c. per sq. cm. per mm. per sec.*

* Gas volumes at atmospheric pressure.

Thus it is seen that oxygen diffuses through tin about 50 times as fast as through silver and that tin diffuses through lead about 1000 times as fast as through silver. Assuming that the rates of diffusion in lead and tin are of the same order of magnitude, it will be seen that the rate of diffusion of oxygen is not significantly greater than the rate of diffusion of metallic elements in the white metals. The data recorded above are taken from the following sources: (1) diffusion of oxygen through tin measured in the Metals Research Laboratory by observing the increase in weight of a sealed tin tube containing a dish of sodium and correcting for external oxidation; (2) diffusion of oxygen through silver extrapolated from the data of Johnson and Larose⁷; (3) diffusion of tin

through lead, Seith and Laird⁸; and (4) diffusion of tin through silver extrapolated from the measurements of Seith and Peretti.⁹

RATES OF OXIDATION OF SILVER-BASE ALLOYS

The depths of the subscales in the silver alloys oxidized at 850°C. are recorded in Table 1. In a previous publication⁶ a method has been described for calculating the rate of subscale growth from known values of the rates of diffusion of oxygen (D_o), and the solute metal (D_m) in the base metal, the solubility of oxygen in the base metal (C_o), the concentration of the solute (C_m), and the oxygen-metal ratio $O:M$ in the oxide formed. In a simplified form the expression used for this calculation is:

$$\frac{X^2}{t} = \frac{2D_oC_o - 1.68 \frac{O}{M} C_mD_M}{\frac{O}{M} C_M + \frac{C_o}{3}}$$

where X is the thickness of the subscale in time t , in seconds. An attempt has been made to calculate the rates of oxidation of several of the silver-base alloys by the use of this formula, which proved quite successful in the case of copper-base alloys; the results are recorded in Table 3. Basic data were obtained from the following sources: D_o , Johnson and Larose⁷; D_m , Seith and Peretti⁹; C_o , Steacie and Johnson¹⁰; the identities of the oxides were assumed.

The calculated rates of subscale thickness

are all too small; in general, about half the observed thicknesses. Since all values are low by about the same amount, it appears that there is probably an error in the value of D_o or of C_o or both; relatively small errors in these constants would materially influence the magnitude of the calculated rates of oxidation.

SUMMARY

A metallographic examination of 20 dilute alloys of silver heated 3 hr. at 850°C. in the air has shown the presence of internal oxidation in alloys containing: Al, As, Bi, Cd, Cu, Fe, Ge, In, Mg, Mn, Ni, Pb, Sb, Si, Sn, Ti, Tl, Zn, and Zr. The oxides form as solid particles frequently in Widmanstätten array except in the alloys of: As, Bi, Pb, Sb, and Tl, where the oxides form molten globules. The alloy with Ni differs from the others; only the β phase oxidizes and no additional precipitate forms in the matrix.

In a similar study of the 40 alloys of cadmium, lead, tin, and zinc, no instances of internal oxidation were found, except in a lead-sodium alloy and in alloys of tin with aluminum and magnesium. The reason for the near absence of internal oxidation in the alloys of these white metals is probably to be found in an unfavorable rate of diffusion of oxygen as compared with that of the solute elements.

ACKNOWLEDGMENT

A major portion of the work on the white-metal alloys was carried out by

TABLE 3.—Rates of Internal Oxidation of Silver Alloys

Solute in Silver	C_M , Weight Per Cent	C_o , Weight Per Cent	$D_o \times 10^{-6}$	$D_M \times 10^{-9}$	Oxide	Depth of Oxidation in 3 Hr. at 850°C., Cm.	
						Calculated	Observed
Cd	2.48	0.0024	1.6	2.16	CdO	0.0139	0.0276
Cu	1.10	0.0024	1.6	0.86	Cu ₂ O	0.0242	0.0945
In	0.73	0.0024	1.6	1.28	In ₂ O ₃	0.0414	0.0809
Sn	2.89	0.0024	1.6	5.13	SnO	0.0180	0.0294
Sb	2.79	0.0024	1.6	3.10	Sb ₂ O ₃	0.0106	0.0235

Mr. H. Markus, formerly of the Metals Research Laboratory and the Bristol-Myers Co. Cooperative Research.

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DISCUSSION

(T. E. Kihlgren presiding)

T. E. KIH LGREN,* Bayonne, N. J.—This question of internal oxidation is of interest to everyone concerned with metals which are susceptible to it. We generally think of internal oxidation as something objectionable and highly to be avoided. At the same time the phenomenon of internal oxidation may conceivably be considered as something that, on occasion, might be diverted to good uses too.

* Research Metallurgist, International Nickel Co.

I noted that the melting of the silver alloys was carried out in a graphite crucible with a borax cover. Was that true also of the copper-base alloys reported in the preceding paper (p. 310).

A. H. GROBE.—The silver was melted in a pure graphite crucible; the copper alloys in clay-graphite.

T. E. KIH LGREN.—But under a borax cover?

A. H. GROBE.—Yes.

T. E. KIH LGREN.—The point I want to leave with you is simply this: In the earlier discussions of the possibility of melt contamination (Dr. Rhines' previous paper on the same subject¹¹) the introduction of impurities through the flux was not brought up. It has been our experience that it is quite possible, when a borax cover is used on a melt, to actually introduce boron into the fusion, particularly if it is melted in contact with carbon. Have any of these melts been analyzed for boron?

A. H. GROBE.—We melted a blank sample, just pure silver, and had it analyzed; there was a spectrographic trace of boron. Since this sample produced no subscale other than the peculiar effect illustrated in the paper, it was supposed that the small amount of boron was oxidized all the way through. It has been our belief that such small amounts of impurities would be oxidized very rapidly at the subscale-metal interface.

¹¹ *Trans. A.I.M.E.* (1940) **137**, 246.

Diffusion Experiments on a Gold-silver Alloy by Chemical and Radioactive Tracer Methods

BY WILLIAM A. JOHNSON,* JUNIOR MEMBER A.I.M.E.

(New York Meeting, February 1942)

It was pointed out in an earlier paper¹ that our understanding of the atomic mechanism by which diffusion occurs in metallic alloys is scarcely in an advanced state. This unsatisfactory condition is the result not of any lack of interest, but of the difficulty of designing experiments that will yield suitable data. The diffusion coefficient of an alloy, measured in the usual way, is simply a number specifying the rate of homogenization of a nonhomogeneous metal; this number, of itself, can furnish neither the rate at which the individual atoms move nor information as to the mechanism by which they move. It does not necessarily follow, however, that such information cannot be obtained, even if the path to be followed is still not clear.

Much success has been attained in the study of diffusion in ionic crystals. A number of experiments, for which there are few counterparts in connection with metals, yield information often indicating a detailed mechanism by which diffusion probably occurs. From such work, quite acceptable theories of lattice imperfections have been developed by Wagner, Schottky, Frenkel, Jost and others.² It is postulated that real crystals of stoichiometric composition contain, in equilibrium, certain imperfections of which the most important types are: (1) vacant cation sites, with an equal number of interstitial ions; (2)

vacant anion sites, with an equal number of interstitial ions; (3) equal numbers of anions and cations in interstitial positions; (4) equal numbers of vacant anion and cation sites.

The classification of a particular crystal according to this scheme then follows from studies of the variation of electrical conductivity with pressure of the electro-negative component surrounding the crystal, with ion size, and with temperature; other physical phenomena, such as the Hall effect, have aided in establishing the classification. The relative mobility of the anion and cation may be determined by chemical analysis of the salt at the electrodes following electrolysis. With such information, and knowing that one ion never occupies the lattice site normally belonging to an ion of opposite sign, it is usually possible to ascertain the diffusion mechanism.

It is clear that the same experiments are not applicable to metal crystals, and substitute experiments that yield as much information have not yet been devised. Much can be learned, however, about the mobilities of the two* kinds of atoms in alloys by the use of radioactive metals as indicators. Only one such experiment has been performed in the past. In 1933, Seith and Keil,³ in an effort to explain the great difference between the rate of diffusion of gold in lead and of lead in lead, measured the rate of diffusion of radioactive lead in a gold-lead

Manuscript received at the office of the Institute Dec. 1, 1941. Issued as T.P. 1429 in METALS TECHNOLOGY, February 1942.

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¹ References are at the end of the paper.

* For convenience the discussion will be limited to binary alloys.

alloy. From the fact that the lead diffused no faster in the alloy than in pure lead, they concluded that gold diffuses interstitially and that gold and lead form an interstitial solid solution; apparently their prediction of the rate of diffusion of radioactive lead in the alloy was based on a mechanism involving a direct interchange of atoms. Wagner,⁴ considering a mechanism in substitutional alloys in which interstitial and hole diffusion were possible, was also forced to conclude that gold dissolves interstitially in lead. The choice of this type of solid solution to explain the experimental data is not a happy one, for, in view of the similarity of atomic radii these two metals would be expected to form a substitutional solid solution; a possible explanation of the finding of Seith and Keil, not requiring an interstitial solid solution, will be given in a later section of this paper.

In the present work, the rate of diffusion along a chemical concentration gradient of an alloy containing 49.2 atomic per cent gold and 50.8 atomic per cent silver has been determined by the usual chemical method; the rates of diffusion of radioactive gold and of radioactive silver also have been determined in chemically homogeneous alloys of the same composition. It has been the purpose of this work to furnish information of a sort not hitherto available concerning diffusion in metals and to suggest ways in which the work might be extended profitably. It was not expected that a unique description of the mechanism involved in the material transport along a chemical concentration gradient could be derived from these experiments alone; however, a more rational choice between the several proposed diffusion mechanisms might result from such data.

EXPERIMENTAL PROCEDURE

Many experimental methods have been devised for measuring diffusion coefficients, each of which may have advantages for the solution of particular problems. In the

present paper, diffusion was studied by chemical analysis and by the use of radioactive gold and radioactive silver as tracers; while the general procedure was much the same in these three cases, important variations were necessary to secure the most favorable circumstances in each instance.

The diffusion specimens for study by chemical analysis were prepared in the following way: Alloys of the desired composition were made by melting pure gold and silver together in a closed graphite crucible. The alloy buttons were hammered, die-pressed and machined to the form of disks $\frac{7}{8}$ in. in diameter and $\frac{1}{8}$ to $\frac{1}{4}$ in. thick. The two flat faces were polished accurately plane and parallel on No. 3-0 polishing paper. Two such disks of measured thickness, one containing approximately 45 atomic per cent gold and the other approximately 55 atomic per cent gold were welded together by heating under pressure in a vacuum or hydrogen furnace at about 850°C. for about 45 min. The welded specimen was then sealed off in a highly evacuated quartz tube and placed in a potentiometrically controlled electric furnace for the diffusion anneal.* After the diffusion anneal, layers of thickness from 0.002 to 0.005 in., parallel to the original interface, were machined off in a lathe. These layers were then analyzed by standard chemical methods and the usual concentration-penetration curve was thus obtained.

Specimens for the measurement of the rate of self-diffusion of gold in the gold-silver alloy were prepared in much the same manner. Radioactive gold, of half-life 2.74 days,⁵ was produced by slow-neutron bombardment of ordinary gold in a cyclotron; the bombardment yields radioactive gold distributed nearly homogeneously in ordinary gold. An alloy was

* The grain size in all the specimens was large, perhaps 3 to 10 grains per square centimeter.

prepared by melting the bombarded gold with ordinary silver in the proper proportion to yield an alloy of 49.2 atomic per cent gold.* A second alloy of the same chemical composition but without radioactive gold was melted and a diffusion specimen was prepared from these two alloys in the manner described above. The diffusion anneal was carried out in argon or nitrogen at atmospheric pressure rather than in sealed-off evacuated tubes as mentioned above. The time saved by this procedure is valuable because of the relatively short half-life of gold. After diffusion, layers were again machined off.

It will be wise to describe in detail the method of measuring the radioactivity of the layers. The activity of the gold was measured with a β -ray counter feeding a scale-of-eight Geiger-Müller circuit. Unfortunately, it was not possible to measure directly the activity of the lathe turnings because of the impossibility of obtaining reproducible geometry; this is a very important consideration, since the activity of a specimen varies inversely as the square of the distance from the counting device. In previous work on the self-diffusion of pure silver,¹ the lathe turnings were dissolved in acid and the activity of the solution—largely γ -ray—measured with a jacket counter. This procedure is not very satisfactory with radioactive gold because its activity—largely β -ray—is too much absorbed by the solution. Instead, the lathe turnings were melted to form a small bead, weighing about $\frac{1}{2}$ gram, which was rolled into a sheet 0.005 in. thick. A small disk, $\frac{9}{16}$ in. in diameter, was punched from the sheet and placed in a special holder so designed that the relation of the disk to the counter tube was always the same. This procedure yielded a satisfactory efficiency and very reproducible data.

* The choice of this exact composition was entirely by chance; a supply of this alloy was available and there was little reason to choose the obvious 50.0 atomic per cent composition.

The activity of the disks prepared from a number of the layers was too great to be counted accurately with the counting equipment used; such layers were diluted by melting a known weight of ordinary gold-silver alloy of the same composition with the lathe chips. The true activity of the layer was then obtained by dividing the measured activity of the disk by the concentration of lathe turnings in the disk. It was impossible, of course, to roll all of the disks to exactly the same thickness, fortunately, because of the high absorbing power of the alloy for the β -ray activity from gold, the unavoidable variations in thickness had no measurable effect on the activity emerging from one face, as was proved by measuring the activity of a disk whose thickness was varied over a considerable range by grinding. Since the counting of the several disks was done over a period of time, a decay correction was made by calculation, using the half-life time of 2.74 days. The counting rate of each disk, with proper correction for dilution and decay, was thus proportional to the concentration of radioactive gold in the layer from which it was made.

The experimental technique employed with specimens containing radioactive silver differed in two important details from those already described. The changes were expedient because the radiation from the silver was more penetrating than that from the gold, because the total activity of the silver was not high, and because the radioactive silver, as produced, contained no ordinary silver. Radioactive silver, initially approximately equal parts of Ag^{105} (half-life 45 days) and Ag^{106} (half-life 8.2 days) was prepared by deuteron bombardment of palladium in a cyclotron.⁶ The radioactive silver—amounting perhaps to 10^{-12} grams—was chemically separated from the palladium as silver chloride, 50 milligrams of ordinary silver being added as a carrier. The silver was recovered as metallic silver by deposition on a silver cathode from a

cyanide solution. An alloy, weighing approximately $\frac{1}{2}$ gram, containing 49.2 atomic per cent gold, was made from this radioactive silver, ordinary silver and ordinary gold. A thin sheet about 0.002 in. thick was then rolled from the active alloy. This was welded, as described above, between two thick disks of nonradioactive alloy of the same chemical composition yielding a composite specimen in which diffusion was again one-dimensional, but in both the positive and negative directions. These specimens were annealed in sealed-off evacuated tubes and sectioned in layers as before.

The liquid jacket counter⁷ mentioned earlier was deemed most satisfactory for counting. Since the alloy is insoluble in ordinary acids, the lathe turnings were melted with excess silver to yield a composition from which the silver could be extracted with nitric acid. Because of the high penetrating power of the γ rays from silver, the activity was proportional to the weight of radioactive silver in the solution; thus in this case the counting rate must be expressed as counts per milligram of silver per second, while for gold the activity may be expressed simply as counts per second. In order to have a comparison between this method of preparing specimens and that previously described for radioactive gold, a specimen with radioactive silver was prepared by the earlier method; the diffusion coefficient obtained agrees well with the other silver data.

As may be inferred from the various techniques employed, no large experimental errors are to be expected. The temperature measurements are believed to be correct within 1°C.; a difference of 1°C. in temperature changes the diffusion coefficients obtained by about 2 per cent. Errors in the measurement of distance should produce an error not greater than perhaps 2 per cent. The statistical error in the measurement of radioactivity ranged from 0.5 to 3 per cent, and should introduce an insignificant error

in the calculated diffusion coefficient. The amount of diffusion that occurred during the welding operation was usually negligible, although a correction was applied for this; the penetration is determined by the product of time and diffusion coefficient, and this product for the welding operation was usually less than 1 per cent of the value for the diffusion anneal. The effect of various other possible errors is difficult to estimate quantitatively, but is believed to be unimportant. The several experimental errors are largely independent of one another and it is probable that the experimental diffusion coefficients are accurate to 4 or 5 per cent.

EXPERIMENTAL RESULTS

Inasmuch as the circumstances under which the several diffusion experiments were carried out differed in a number of respects, the appropriate solutions of the diffusion equation

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right) \quad [1]$$

to be employed might be expected also to be different. A variation in the diffusion coefficient D with composition could occur only in those specimens having a chemical concentration gradient, and fortunately in these cases the variation of D with composition was too slight to be detected.* Thus, in every case it was possible to rewrite Eq. 1 in the simpler form

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad [2]$$

The proper solution of this equation for specimens made from two thick disks† (those for study by chemical analysis, those containing radioactive gold, and one con-

* Diffusion specimens covering a wider range of compositions might show an appreciable variation of D with composition.

† For convenience, these will be denoted as type A specimens.

taining radioactive silver) is

$$\frac{c - c_0}{c_1 - c_0} = \frac{1}{2} \left[1 - \phi \left(\frac{x}{\sqrt{Dt}} \right) \right] \quad [3]$$

For diffusion in a chemical concentration gradient, c_1 is the initial concentration of

using the value of D that gave the best fit between the calculated curve and the data. The satisfactory agreement between the data and the calculated curve indicates that the diffusion coefficient is substantially independent of composition over this range.

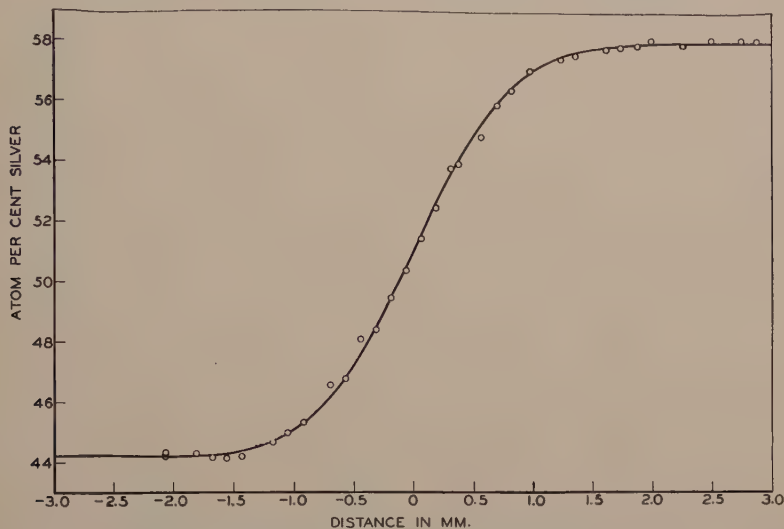


FIG. 1.—CONCENTRATION-PENETRATION CURVE FOR DIFFUSION IN CHEMICAL CONCENTRATION GRADIENT AT 965.4°C. FOR 4.02 DAYS.

silver in the high concentration alloy, c_0 is the initial concentration of silver in the low concentration alloy, c is the concentration of silver after a time t at a distance x from the interface, ϕ is the probability integral and D is the diffusion coefficient; all concentrations are in atomic per cent. For chemically homogeneous specimens, c_1 is the maximum counting rate, c_0 is zero, and c is the counting rate at a distance x from the interface.

Fig. 1, which is characteristic of the experimental results on specimens with a chemical concentration gradient, is a concentration-penetration curve obtained from a specimen heated at 965.4°C. for 4.02 days; the initial concentrations at the ends of the specimen were, respectively, 44.19 and 57.93 atomic per cent silver. The circles are experimental points and the smooth curve was calculated from Eq. 3,

The type of curve shown in Fig. 1 is not the most convenient for calculating the diffusion coefficient. A special type of graph paper known as "probability" paper may be used very advantageously.* On this paper, any data accurately satisfying Eq. 3

* Such paper may be purchased, but with difficulty; it may be laid out on ordinary graph paper in the following way: Distances are plotted linearly as abscissas; the values of y satisfying the relation

$$2z = 1 - \phi(y)$$

are calculated for a series of values of z ranging from 0 to 1; each value of y thus obtained is marked off on the ordinate axis and labeled with the corresponding value of z ; then the value of z corresponding to a given concentration c is obtained from the relation

$$z = \frac{c - c_0}{c_1 - c_0}$$

and in this way a point having any values of c and x may be plotted.

will plot as a straight line whose slope depends only on the product Dt . The paper thus furnishes not only a rapid method for determining the value of D but also an

Fig. 3 is a plot on probability paper of a concentration-penetration curve obtained with radioactive gold in a chemically homogeneous specimen heated at 963.1°C . for

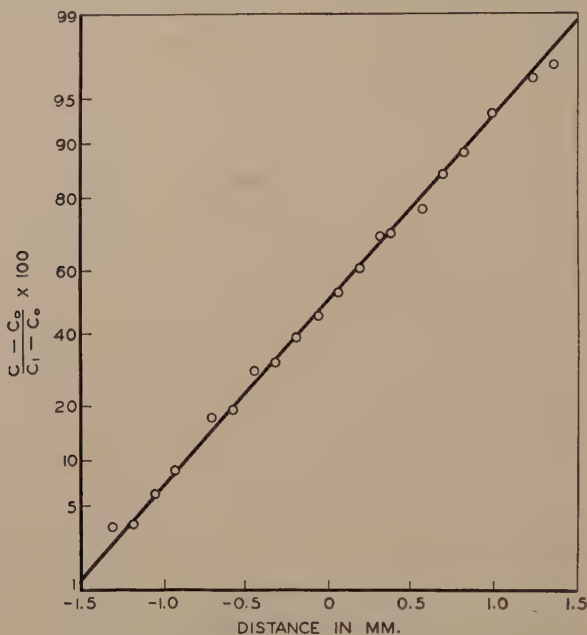


FIG. 2.—RELOT ON PROBABILITY PAPER OF DATA FROM FIG. 1.

accurate test of the constancy of D with composition, for if D varies with composition a straight line will not result. The experimental points shown in Fig. 1 have been replotted on probability paper in Fig. 2; it is apparent that they lie quite satisfactorily along a straight line. Some caution must be used in applying this type of plot, however, because the scale is greatly extended at the ends and there is usually no corresponding increase in the accuracy of analysis. Since analyzed compositions less than c_0 or greater than c_1 cannot be plotted, the data will always appear to deviate systematically from a straight line at the ends because of slight errors in chemical analysis. Bearing this in mind, in drawing a line through the data, only the compositions lying between 5 and 95 per cent of the whole composition range were considered.

1.58 days. As in Fig. 2, the experimental points fall accurately along a straight line. The concentration range covered in Fig. 3 is much greater than that in Fig. 2; in view of the remarks made above concerning the inadvisability of plotting too great a concentration range on probability paper, a brief comparison of the accuracies obtainable in chemical analysis and radioactivity measurement is in order. The accuracy of chemical analysis in the present work was about ± 0.15 per cent, or about ± 1 per cent of the composition range employed; this accuracy was independent of composition. Circumstances are rather different in the measurement of radioactivity, for the accuracy depends not alone on the personal factor but also on statistical fluctuations in the emitted activity. Thus, no matter how refined the experimental technique, there is

always a probable error in the measured activity of approximately the square root of the number of counts. With counting rates limited to perhaps 500 to 1000 counts per

coefficient. It is clear, then, that the *effective* accuracy of radioactivity measurements under the circumstances obtaining in the present work may be very high at the low

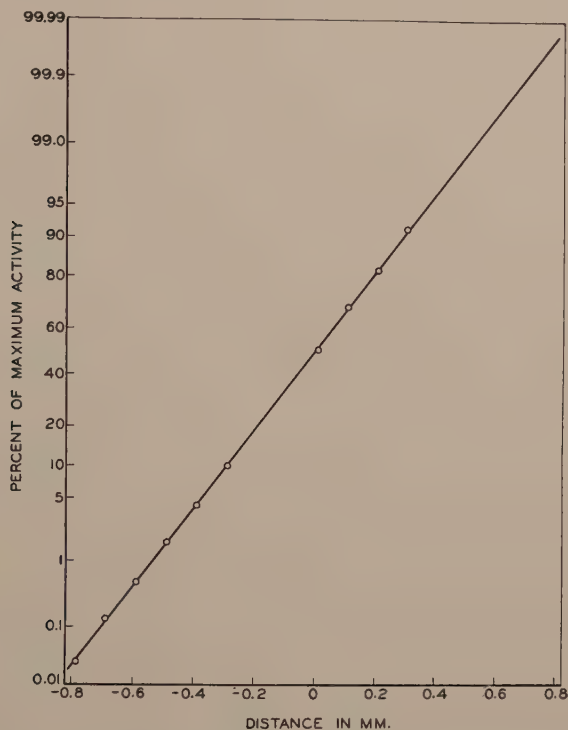


FIG. 3.—CONCENTRATION-PENETRATION CURVE ON PROBABILITY PAPER FOR DIFFUSION OF RADIOACTIVE GOLD IN A GOLD-SILVER ALLOY AT 963.1°C. FOR 1.58 DAYS.

minute, inconveniently long times are necessary to obtain probable errors of less than say 0.5 per cent (40,000 counts); often the counting rate is much lower than this, and probable errors as high as 3 per cent may be unavoidable. It is to be noted, however, that these probable errors are based on the measured values and have no relation to the total composition range, as in chemical analysis. Thus a probable error of 3 per cent in a layer having an activity of 0.1 per cent of the maximum produces a variation of only ± 0.003 per cent when referred to the whole concentration range; it is the ± 0.003 per cent variation that is important in calculating the diffusion

concentrations. At high concentrations the *effective* accuracy is much poorer (even though the probable error may be much smaller) and thus data for the high concentrations are omitted from Fig. 3.*

The proper solution of Eq. 2 for the boundary conditions employed in most of the experiments with radioactive silver (type B specimen) is

$$c = \frac{c_0}{2} \left[\phi \left(\frac{x+b}{2\sqrt{Dt}} \right) - \phi \left(\frac{x-b}{2\sqrt{Dt}} \right) \right] \quad [4]$$

* Under other experimental conditions, the effective accuracy of chemical analysis may be much improved, as by the use of the polarograph for very dilute solutions.

where c_0 is the initial concentration of radioactive silver in the central layer of thickness $2b$, and the other symbols have their former meaning.

If the condition be imposed that the two terms in the brackets are small compared to unity, on taking logarithms of Eq. 5 and using a series expansion for the logarithm of

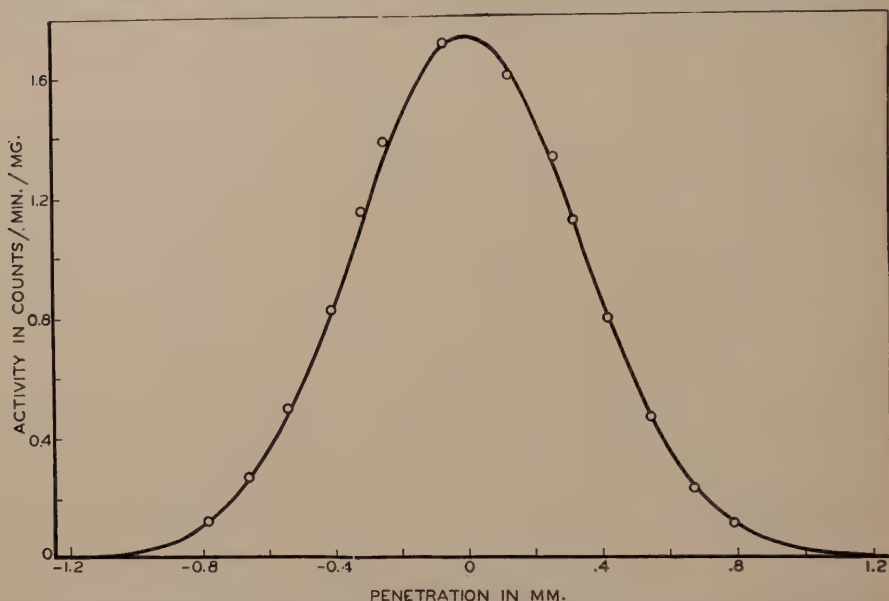


FIG. 4.—CONCENTRATION-PENETRATION CURVE FOR DIFFUSION OF RADIOACTIVE SILVER IN A GOLD-SILVER ALLOY AT 813.4°C. FOR 17.69 DAYS.

Fig. 4, which is characteristic of the experimental data on specimens of this type, is a concentration-penetration curve obtained from a specimen heated at 813.4°C. for 17.69 days. The circles are experimental points and the smooth curve was calculated from Eq. 4, using the value of D that gave the best fit between the calculated curve and the data; again the agreement is satisfactory.

It is very inconvenient to determine D from Eq. 4. The calculation may be greatly simplified by using an approximate equation, which is very accurate for the values of x , b , D and t obtaining in the present work. If the right-hand side of Eq. 4 is expanded by a Taylor's series, neglecting derivatives higher than the fourth,

$$c = \frac{bc_0}{\sqrt{\pi Dt}} e^{-\frac{x^2}{4Dt}} \left(1 - \frac{b^2}{12Dt} + \frac{b^2 x^2}{24D^2 t^2} \right) \quad [5]$$

the term in brackets, the simple relation

$$\log c = \log k - 0.1086 \frac{x^2}{Dt} \left(1 - \frac{b^2}{6Dt} \right) \quad [6]$$

is obtained, where the constant k need not be specified for the present purpose.

If the logarithm of the radioactivity is plotted as a function of the square of the distance from the interface, the data will be expected to lie along a straight line, and this expectation is accurately fulfilled (Fig. 5). The slope of this line, according to Eq. 6, is

$$\text{slope} = - \frac{0.1086}{Dt} \left(1 - \frac{b^2}{6Dt} \right) \quad [7]$$

and since b and t are known, D is calculated readily.*

* The accuracy of Eq. 6 becomes poorer as the value of the term $\frac{b^2}{6Dt}$ increases; in the most unfavorable case in the present work, its value was only 0.02 and the error of the approximation is certainly negligible.

All of the calculated diffusion coefficients are slightly too small, since diffusion distances are shorter at room temperature, where measurements were made, than at the diffusion temperature. The proper correction is readily calculated from the coefficient of thermal expansion of the alloy and varies from 2.6 per cent at 725°C. to 3.5 per cent at 950°C.

The various diffusion coefficients, with pertinent data, are given in Table I.

TABLE I.—*Summary of Experimental Diffusion Data*

Test No.	Specimen Type	Concentration Gradient	<i>b</i> , Cm.	Temperature, Deg. K.	Time, Days	<i>D</i> , ^a Sq. Cm. per Sec.
1	B	Radioactive silver	0.004	1240.8	4.52	5.41×10^{-9}
2	B	Radioactive silver	0.004	1162.6	7.07	1.49×10^{-9}
3	B	Radioactive silver	0.004	1086.6	17.69	3.84×10^{-10}
4	B	Radioactive silver	0.0043	999.4	37.19	6.69×10^{-11}
5	A	Radioactive silver		1238.1	3.99	5.06×10^{-9}
6	A	Chemical		1238.6	4.02	6.56×10^{-9}
7	A	Chemical		1159.9	7.86	1.94×10^{-9}
8	A	Chemical		1065.4	19.06	3.88×10^{-10}
9	A	Chemical		989.8	32.71	9.24×10^{-11}
10	A	Radioactive gold		1236.3	1.58	1.94×10^{-9}
11	A	Radioactive gold		1130.2	11.60	3.42×10^{-10}
12	A	Radioactive gold		1040.8	15.30	6.68×10^{-11}

^a The diffusion coefficient in every case is at the composition of 50.8 atomic per cent silver, 49.2 atomic per cent gold.

It has become customary to represent the variation of the diffusion coefficient with temperature by plotting the logarithm of *D* as a function of the reciprocal of the absolute temperature. The data in Table I have been plotted in this fashion in Figs. 6, 7 and 8. In such plots, experimental data for metals usually fall along a straight line; if this is the case, the equation of such a line may be written

$$D = Ae^{-\frac{Q}{RT}} \quad [8]$$

where *Q* is the activation energy for diffusion. In a few cases of metallic diffusion and quite often in ionic diffusion the data cannot be represented over a large temperature range by one exponential term, but are well reproduced by two or more such terms.

Fig. 6 shows the temperature variation of the diffusion coefficient *D_c*,* measured

chemically, together with such other data for this system as are available. The values determined in the present work lie close to a straight line whose equation is:

$$D_c = 0.14e^{-\frac{41700}{RT}} \text{ sq. cm. per sec.} \quad [9]$$

A close examination of Fig. 6 reveals that the data deviate systematically from this straight line by an amount approximating the experimental error; the nature of this

deviation suggests that the data might preferably be represented by an equation of the form

$$D = A_1e^{-\frac{Q_1}{RT}} + A_2e^{-\frac{Q_2}{RT}} \quad [10]$$

but since it is not certain that these deviations are significant, the simpler straight line has been chosen for the present. The rather poor agreement among the several sets of data demands explanation. The work of Weiss and Henry,⁸ Fraenkel and Houben,⁹ and perhaps Jost,¹⁰ is open to objection because of the use of chemical etch-limit methods of doubtful validity.* These experiments, even if not in error in this respect, yielded only an ill-defined average diffusion coefficient over a composition range from pure gold to pure silver; it is to be expected that such data

* Hereinafter, the chemically measured rate of diffusion will be denoted by the symbol *D_c*.

* Jost's data were obtained at low temperatures and were extrapolated by him to agree with Braune's at high temperatures.

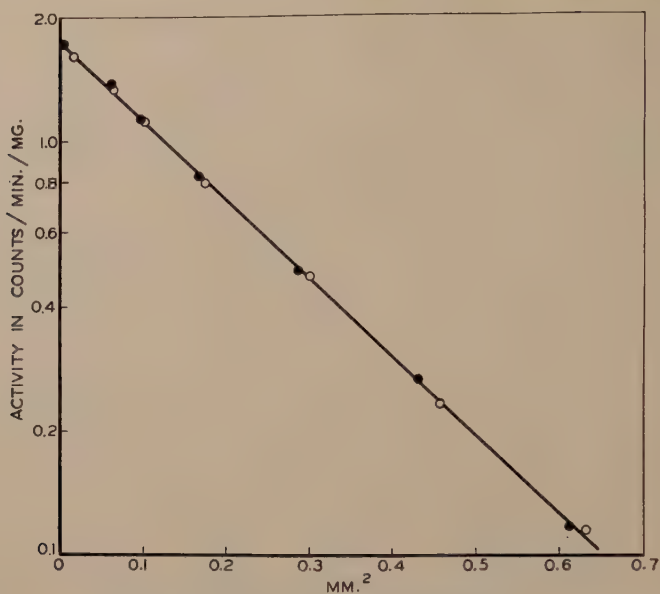


FIG. 5.—RELOT OF DATA FROM FIG. 4.

Log radioactivity as ordinate and distance from interface squared as abscissa; open circles from right side of Fig. 4, closed circles from left side.

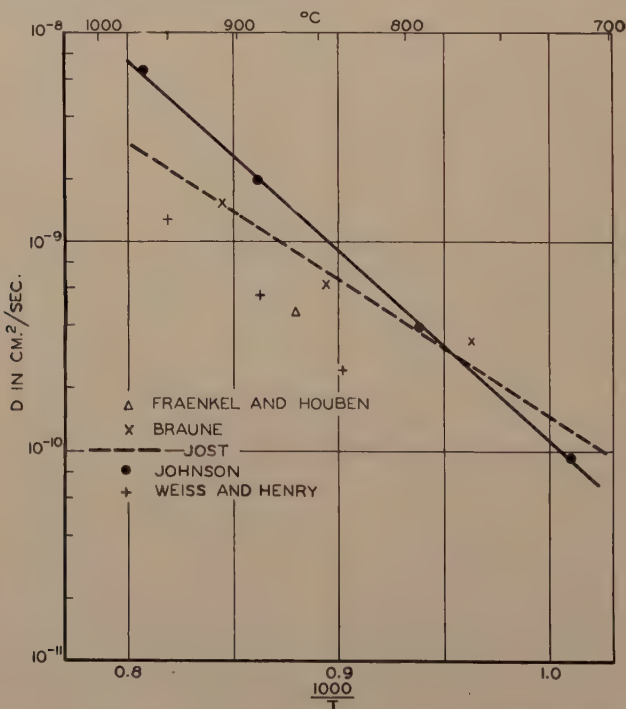


FIG. 6.—VARIATION OF CHEMICAL DIFFUSION COEFFICIENT WITH TEMPERATURE, LOGARITHM OF D VERSUS RECIPROCAL OF ABSOLUTE TEMPERATURE.

will not agree with those taken over a narrow composition range. The diffusion coefficients originally given by Braune, who employed a satisfactory chemical method, were all too high by a factor of four through a misapplication of the Stefan-Kawalki tables.

The diffusion coefficient of radioactive silver in a chemically homogeneous gold-silver alloy, D_{Ag} , is shown at several temperatures in Fig. 7; the second curve shown in this graph is the self-diffusion coefficient of pure silver.¹ It is perhaps rather surprising, in view of past concepts concerning the loosening of a lattice by the introduction of foreign atoms, that the two lines should be so similar; the relation here is apparently analogous to the previously mentioned behavior of the lead-gold system. The data again deviate systematically from a straight line and to the same extent; however, a simple exponential equation has been chosen to represent the diffusion coefficient:

$$D_{Ag} = 0.39e^{-\frac{44700}{RT}} \text{ sq. cm. per sec.} \quad [11]$$

A similar comparison is not made for the diffusion of radioactive gold in a chemically homogeneous alloy, because the self-diffusion coefficient of gold is not known with good accuracy, although some data are available.^{11,12} The temperature dependence of the rate of diffusion of radioactive gold in a homogeneous alloy, D_{Au} , is shown in Fig. 8, and may be represented by the equation:

$$D_{Au} = 0.12e^{-\frac{44100}{RT}} \text{ sq. cm. per sec.} \quad [12]$$

The rate of diffusion of gold in the alloy is about 20 times greater than the reported rate of self-diffusion of gold.

The interrelation of the three diffusion-rate curves shown in Fig. 8 will be considered in a later section of this paper.

VOLUME CHANGES DURING DIFFUSION

When specimens employed in determining the rate of chemical diffusion were

examined after the diffusion anneal, it was noticed that a small but quite regular volume change had occurred. This consisted of an increase in diameter in the high-gold side, and a contraction in diameter on the low-gold side, both dilatations appearing near the original interface. A somewhat similar phenomenon was observed by Fraenkel and Houben⁹ with specimens made by hammering a silver wire into a hole in a gold block. They believed the volume changes to be caused by the difference in thermal expansion of gold and silver, but the effect is far too great in magnitude to be produced by this alone. The two most plausible explanations for this behavior are: (1) evaporation of silver from the alloy high in silver and condensation on the alloy low in silver; (2) more rapid diffusion of silver out of the high-silver alloy than of gold into it. If the second possibility* occurred to any appreciable extent, its study would furnish very important information about the diffusion mechanism, for, unless the theories of lattice imperfections are incorrect, such a process would require marked interstitial diffusion. It was thought that the first of these possibilities was the more probable and thus an experiment suitable for testing this was designed.

Two specimens were prepared by welding relatively thick gold and silver disks together (specimen type A). One of these was annealed at 943°C. in argon at atmospheric pressure for a total of 6 hr., 24 hr., 54 hr. and 96 hr. successively and the contour of the surface measured. The contour after 96 hr. is shown in Fig. 9. A comparison of the dilatations after the various annealing times showed that the change in diameter increased linearly with time, which is to be expected if evaporation is the controlling factor. The surface of the silver had been etched by evaporation but the surface of the gold—away from the interface—was apparently unchanged. Since the vapor pressure of silver at the temperature

employed is appreciable but not high and is roughly 10^5 times as great as that of gold, it is not surprising that vacuum etching of gold did not occur; because of the atmos-

ings, it is believed that the volume change was produced entirely by evaporation (with perhaps an insignificant change caused by differential expansion) and that there is no

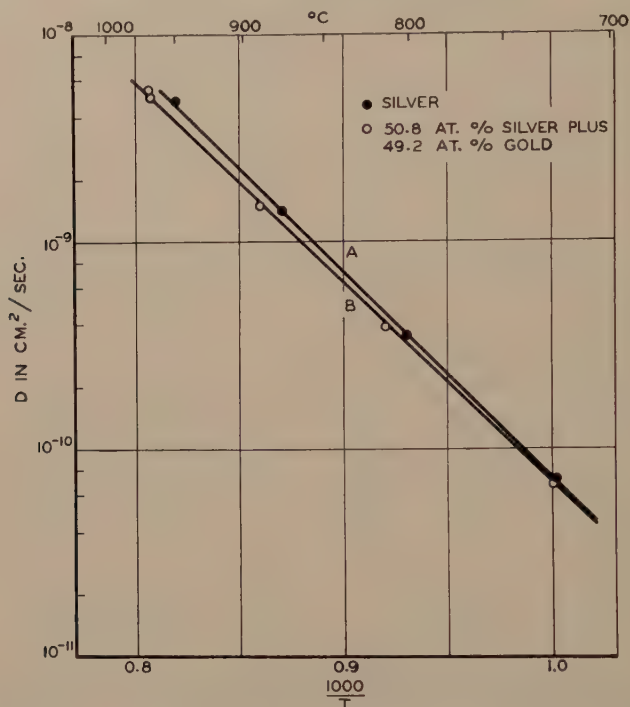


FIG. 7.—VARIATION OF SELF-DIFFUSION COEFFICIENT OF SILVER WITH TEMPERATURE IN PURE SILVER AND IN A SILVER-GOLD ALLOY. LOGARITHM OF D VERSUS RECIPROCAL OF ABSOLUTE TEMPERATURE.

phere of argon around the specimen, the mean free path of the evaporated silver atoms was too short for their movement to the distant parts of the gold surface. The second specimen was heated in a continuously pumped vacuum for 6 hr. at the same temperature. Its contour after this treatment is shown also in Fig. 9. It is clear that a much greater volume change occurred in this case in only $1/16$ of the time; the surface of the gold end of the specimen was everywhere a light yellow color, showing the presence of perhaps 50 atomic per cent silver, and the diameter was markedly increased far beyond the zone of appreciable diffusion. On the basis of these find-

reason to suspect that it may have been the result of diffusion.

DISCUSSION OF RESULTS

A consideration of the wide diversity of experiments that necessarily have been employed in establishing the mechanism of diffusion in ionic crystals indicates that even though data of a new sort have been made available in metals by the radioactive tracer technique, it is still not possible to arrive immediately at the atomic mechanism sought. Thus it appears that rather than attempt to ascertain this mechanism directly, more rapid progress will be made if the more attractive diffusion theories that

have been proposed¹³ are examined in the light of these and similar experiments.

Perhaps the most surprising feature of the experimental data is that the chemically

extreme case consider, for example, a lattice in which the gold atoms are immobile on their lattice positions; the analogous situation occurs in ionic lattices.

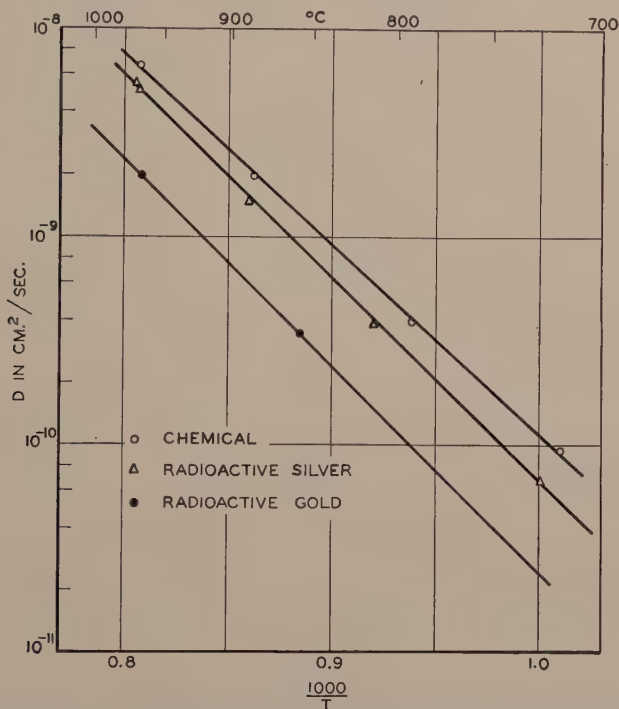


FIG. 8.—VARIATION WITH TEMPERATURE OF SELF-DIFFUSION COEFFICIENT OF SILVER AND OF GOLD, AND OF CHEMICAL DIFFUSION COEFFICIENT, IN A SILVER-GOLD ALLOY, LOGARITHM OF D VERSUS RECIPROCAL OF ABSOLUTE TEMPERATURE.

measured rate of diffusion is more rapid than the self-diffusion rate of either silver or gold; considering the process in general terms, it would appear that the opposite behavior is to be expected. Since in a substitutional alloy the same number of atoms must move to the right as to the left, a silver atom, for example, moving to the right must have its movement balanced by the movement of either a gold or a silver atom to the left; only the movement of a gold atom in the opposite direction will result in a chemically measurable diffusion, but the motion of either kind of atom in the opposite direction results in a diffusion measurable by the tracer method. As an

Then there is never any chemically measurable change in the specimen, but the motion of the silver is clearly revealed by tracer technique. Thus in this case

$$\begin{aligned} D_{Ag} &> 0 \\ D_c &= D_{Au} = 0 \end{aligned}$$

Since the data contained herein do not stand in the predicted relation, the argument is clearly fallacious.

While one might try to discover the fallacy in the preceding argument by an equally general, and perhaps equally misleading, discussion, it will be more convincing to show that these predictions are not necessarily fulfilled in either of two

simple diffusion mechanisms. We shall assume first the simplest type of mechanism that is at all reasonable—the direct interchange of atoms in an ideal lattice dis-

where δ is a distance depending on the lattice type and size, τ_{AgAu} is the mean time of interchange of gold and silver atoms once they have acquired sufficient energy, and

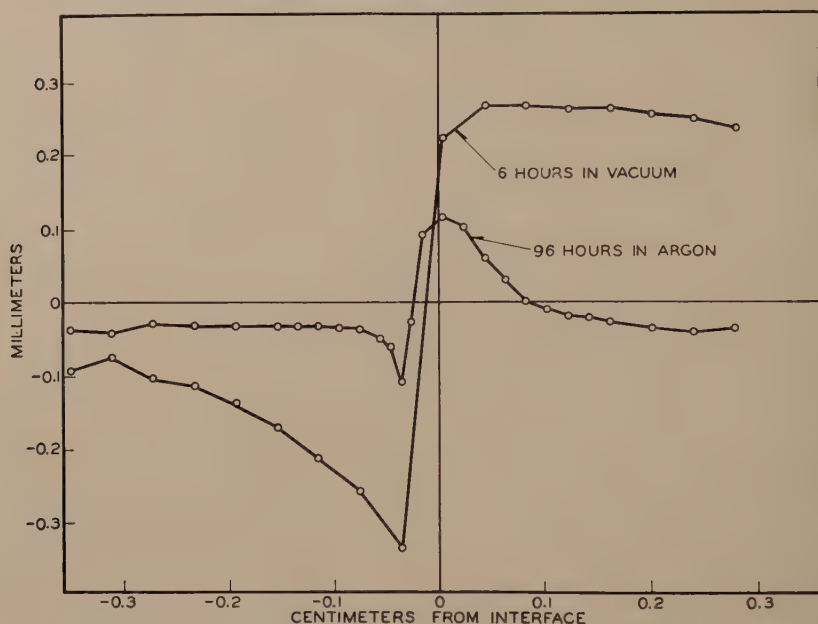


FIG. 9.—EFFECT OF ATMOSPHERE ON VOLUME CHANGES OCCURRING DURING DIFFUSION. Gold on right side of interface, silver on left.

cussed by Dorn and Harder.¹⁴ By the straightforward but rather qualitative procedure employed by them, it is possible to derive the following equations for the three diffusion coefficients of interest here:*

$$D_c = \frac{\delta^2}{\tau_{AgAu}} e^{-\frac{(Q_{Ag} + Q_{Au})}{RT}} \quad [13]$$

$$D_{Ag} = \frac{\delta^2}{\tau_{AgAg}} c_{Ag} e^{-\frac{2Q_{Ag}}{RT}} + \frac{\delta^2}{\tau_{AgAu}} c_{Au} e^{-\frac{(Q_{Ag} + Q_{Au})}{RT}} \quad [14]$$

$$D_{Au} = \frac{\delta^2}{\tau_{AuAu}} c_{Au} e^{-\frac{2Q_{Au}}{RT}} + \frac{\delta^2}{\tau_{AgAu}} c_{Ag} e^{-\frac{(Q_{Ag} + Q_{Au})}{RT}} \quad [15]$$

* It is interesting to note that many diffusion problems may be studied to advantage also by the method of the "random walk" considered in gas kinetics.¹⁶

which depends on the vibrational frequency of the atoms and their arrangement in the crystal, Q_{Ag} is the energy required to loosen a silver atom, and c_{Ag} is the atom concentration of silver; the meaning of the other terms is easily inferred by analogy. In the present case c_{Ag} and c_{Au} are both very nearly 0.5, so that the equations may be more conveniently written:

$$D_c = D_c \quad [16]$$

$$D_{Ag} = 0.5D_{AgAg} + 0.5D_c \quad [17]$$

$$D_{Au} = 0.5D_{AuAu} + 0.5D_c \quad [18]$$

These equations place no upper limit on D_{Ag} and D_{Au} but do place the lower limit of $0.5D_c$;^{*} the initial argument is thus seen to be incorrect. Fig. 8 shows that D_{Ag} is greater than $0.5D_c$, but D_{Au} is less than

* While the derivation is admittedly qualitative, it is very probable that the minimum values of D_{Ag} and D_{Au} are correct.

$0.5D_c$. However, and perhaps unfortunately, it cannot be assumed that these data preclude the possibility of direct interchange as the predominant diffusion

solute atoms. It will not be attempted here, for a number of assumptions must be made, of which the nature is still uncertain; when data showing the variation of D_c , D_{Ag} and

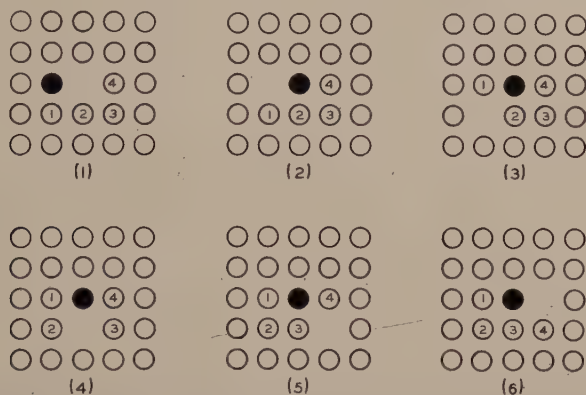


FIG. 10.—SCHEMATIC REPRESENTATION OF CYCLE BY WHICH SOLUTE-HOLE MOLECULES DIFFUSE.

mechanism, for with a suitable—and not unreasonable—variation in Q_{Ag} and Q_{Au} with composition, the minimum value of D_{Au} may fall below that given in Eq. 18. This variation would have to be simply that less energy would be required for a gold atom to jump toward lower gold concentrations than toward higher. It should be mentioned, however, that energy considerations are thought to make the direct interchange mechanism improbable.¹⁶

The possibility of interstitial diffusion will not be entertained, for it appears to be energetically very improbable in a lattice with atoms of equal size.^{17,18} We should note, however, that even if this mechanism operated it would have to be of a very special type, neither like that occurring in ionic crystals nor like that occurring, for example, when carbon diffuses into iron, for only a small fraction of the atoms could occupy interstitial positions and, with usual mechanisms, large concentration changes could not occur.

Unfortunately, a detailed consideration of hole diffusion, which appears energetically most probable, is very difficult in alloys containing a large concentration of

D_{Au} with composition are available, however, it is probable that a satisfactory analysis can be completed.

On the other hand, some rather interesting conclusions can be reached concerning diffusion in dilute alloys by employing the solute-hole molecule suggested by R. P. Johnson.¹⁹ In most discussions of diffusion by the hole mechanism, the holes are assumed to form statistically in the lattice, which, as Johnson points out, limits the rate of diffusion of the solute atoms to the rate at which holes diffuse to them from the hinterlands of the crystal. The cyclic mechanism by which the solute-hole molecule wanders randomly through the lattice is illustrated in Fig. 10, in which the solid circle represents the foreign atom and the solvent atoms involved in the process are numbered for identification. It is clear that for the movement of the solute atom one unit distance in a specified direction, several solvent atoms must move; it should not be inferred, however, that the solvent atoms are in general more mobile than the foreign atom. The solute-hole molecule may wander large distances by this mechanism, but the solvent atoms, after contributing to

this single cycle, will not move again until another solute-hole molecule diffuses to them. This will occur but rarely in a dilute alloy, and thus the chemical diffusion coefficient and the rate of self-diffusion of the solute may be fairly high but the rate of self-diffusion of the solvent may be not appreciably higher than that of the pure metal; the data of Seith and Keil are in agreement with these arguments.*

It is clear that the experiments reported here are alone not sufficient to determine the atomic mechanism of diffusion. With additional experiments of this type, perhaps others of a sort not yet devised, and with a careful mathematical study of the processes, however, it is probable that the goal sought will be attained.

SUMMARY

The chemically measured rate of diffusion in an alloy containing 49.2 atomic per cent gold and 50.8 atomic per cent silver has been found to be

$$D_c = 0.14e^{-\frac{41700}{RT}} \text{ sq. cm. per sec.}$$

The diffusion rate of silver in the same alloy is

$$D_{Ag} = 0.39e^{-\frac{44700}{RT}} \text{ sq. cm. per sec.}$$

and the diffusion rate of gold in the same alloy is

$$D_{Au} = 0.12e^{-\frac{44100}{RT}} \text{ sq. cm. per sec.}$$

Several of the more probable diffusion mechanisms are discussed in the light of these data.

ACKNOWLEDGMENT

It is a pleasure to thank Dr. A. A. Bates, Dr. E. U. Condon and Dr. R. F. Mehl for their interest in this work, and to thank

* No attempt has been made to treat this case mathematically; it is not improbable that the rate of diffusion of lead should be increased somewhat by the addition of gold.

Dr. Martin Kamen, who prepared the radioactive gold in the cyclotron of the University of California.

The experimental work was made possible through the support of the Westinghouse Research Laboratories and the Metals Research Laboratory of the Carnegie Institute of Technology.

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DISCUSSION

(M. A. Hunter presiding)

E. O. KIRKENDALL,* Detroit, Mich.—In discussing chemically measured diffusion, Dr. Johnson gave an explanation for the volume change, which may be its major cause. However, it was a little disappointing to have him say: "... there is no reason to suspect that the volume change may have been the result of diffusion." If the silver diffuses more rapidly than the gold, as shown by the radioactive tracer method, there will be a slight volume change and a shift in the interface to provide room for the silver atoms that have crossed the interface without a simultaneous diffusion of gold atoms in the opposite direction. The gold atoms may appear to be diffusing at the same rate as the silver atoms, while actually the gold atoms and the interface are being

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pushed around to provide room for the more rapidly diffusing silver atoms.

If the interface does shift, it would be necessary to recalculate the rate of diffusion as measured chemically by Dr. Johnson. To use a crude analogy, one cannot measure the land speed of an airplane flying against a head wind and tell its true speed capabilities without knowing the wind velocity. It may not be possible to measure the shift in the interface from Dr. Johnson's data, but estimating it might give a diffusion coefficient for silver in a fifty-fifty gold-silver alloy which could be correlated with that found by radioactive tracer methods.

M. S. MAIER,* Columbus, Ohio.—What is the physical significance of the value of the diffusion coefficient D as determined from the concentration-penetration curve obtained by chemical analysis, Fig. 1? Is it to be considered as the coefficient of silver diffusing into the gold-rich gold-silver alloy, or that of gold diffusing into the silver-rich alloy, or possibly the sum of the two? The normal procedure of determining diffusion coefficients from such a concentration-penetration curve is to start at an interface and determine a diffusion coefficient representing the rate of flow of solvent atoms across the interface into the solvent metal. In the present work, the author apparently has used the entire concentration-penetration curve and from it determined a single value for D , the physical significance of which is not designated.

In Fig. 8 is shown the variation of the three diffusion coefficients, obtained in this work, with temperature. I note that at any temperature the diffusion coefficient D , obtained by chemical analysis, is very nearly equal to the sum of the individual diffusion coefficients obtained using radioactive gold and radioactive silver. Could this be interpreted that the D obtained by chemical analysis is the sum of the diffusion coefficients of radioactive silver into the alloy and radioactive gold into the alloy, or is it just a coincidence?

It is interesting to note the similarity between the rate of diffusion of radioactive silver into

the gold-silver alloy and the rate of self-diffusion of silver as shown in Fig. 7. Is there any like similarity between the rate of diffusion of radioactive gold into the gold-silver alloy and the published rates of self-diffusion of gold?

W. A. JOHNSON (author's reply).—It is unfortunate that Dr. Kirkendall's interesting suggestion that there should be a gross movement of the interface during diffusion in gold-silver alloys cannot be tested by any of the data available to the author. This idea arises, perhaps, from the behavior observed by Dr. Kirkendall in copper: β -brass diffusion couples, but the phenomenon has not been found often enough to be considered general.

We should emphasize, however, that Dr. Kirkendall is not justified in concluding that there must be a volume change because the diffusion coefficients of gold and silver differ. A shift of the interface will occur only if the *net* flow of gold atoms in the one direction is not equal to the *net* flow of silver atoms in the other. As was pointed out in the text, D_{Au} and D_{Ag} may differ considerably; for example, in a direct atom interchange mechanism where no volume change can occur. Thus Dr. Kirkendall's suggestion and the one given in the paper, while quite different, are both consistent with the data available. The author still prefers his original view, since it is in better accord with prevailing ideas concerning the diffusion mechanism of lattice vacancies.

The answers to most of the questions asked by Dr. Maier may be found in the text of the paper; it is apparent, however, that certain of these points were not discussed adequately. The method employed for calculating the chemical diffusion coefficient is quite normal. The use of the whole penetration curve instead of a single point yields an average D for all the experimental data rather than a value based on a single point; the diffusion coefficient thus determined is exactly the coefficient always measured in experiments of this sort, and specifies the rate of homogenization of the diffusion couple. It is true, as Dr. Maier observes, that the sum of D_{Ag} and D_{Au} nearly equals D_c , but this must be regarded merely as a coincidence.

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A New Method for Determination of Stress Distribution in Thin-walled Tubing

BY G. SACHS,* MEMBER, AND G. ESPEY,† STUDENT ASSOCIATE A.I.M.E.

(Philadelphia Meeting, October 1941)

THEORY OF STRESS MEASUREMENT IN THIN-WALLED TUBING

APPROXIMATION METHODS FOR MEASUREMENT OF STRESSES IN THIN-WALLED TUBING

SIMPLE methods can be used for the determination of the residual stresses in thin-walled tubing if the stresses consist of high tensile stresses at the one surface and high compressive stresses at the other surface. Such a stress distribution is approximated in sunk tubing and in deep-drawn shells. It is possible to cut sections from such articles in such a manner that a major part of the residual stress is relieved by a bending of the part that is separated from the adjacent metal.

The circumferential stress is evaluated from the change in diameter D , occurring on splitting a length of tubing (Fig. 1b),¹⁻⁵ or from deflection resulting from the cutting out of a circumferential tongue (Fig. 1a).⁶ The bending moment M released by such a flexure is:

$$M = \frac{EI}{1 - \nu^2} \left(\frac{1}{R_0} - \frac{1}{R_1} \right) = \frac{EI}{1 - \nu^2} \frac{R_1 - R_0}{R_0 \times R_1}$$

where E = modulus of elasticity,

ν = Poisson's ratio,

I = moment of inertia of the section,

R_0 = mean radius before splitting,

R_1 = mean radius after splitting.

The release of this bending moment corresponds to the release of stresses, which, in a thin section, vary linearly from one surface to the other, and have the following value in a particular fiber a certain distance (x) from the surface:

$$S = \frac{M}{C} \frac{\left(\frac{d}{2} - x\right)}{\frac{d}{2}} = \frac{E}{1 - \nu^2} \times \frac{I}{C} \times \frac{\left(\frac{d}{2} - x\right)}{\frac{d}{2}} \times \frac{R_1 - R_0}{R_0 \times R_1} = \frac{E}{1 - \nu^2} \left(\frac{d}{2} - x\right) \frac{R_1 - R_0}{R_0 \times R_1}$$

where C is the section modulus and d is the thickness of the section, the ratio $M:C$ being $d:2$ for a rectangular section.*

The maximum stress values at the surfaces are:

$$S_{\max} = \pm \frac{E}{1 - \nu^2} \times \frac{d}{2} \times \frac{R_1 - R_0}{R_0 \times R_1}$$

For most purposes the simpler equations:

$$S_{\max} = \pm \frac{E}{1 - \nu^2} \times \frac{d}{2} \times \frac{R_1 - R_0}{R_m^2} = \pm \frac{E \times d}{1 - \nu^2} \times \frac{\Delta D_1}{D_m^2}$$

and

$$S = \frac{E}{1 - \nu^2} (d - 2x) \times \frac{\Delta D_1}{D_m^2}$$

will be satisfactory, where D_m is the average of the mean diameters of the tubing

Manuscript received at the office of the Institute July 7, 1941. Abstracted from a thesis presented to the Case School of Applied Science by G. Espey in partial fulfillment of the requirements for the M. S. degree. Issued as T.P. 1384 in METALS TECHNOLOGY, October 1941.

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¹ References are at the end of the paper.

* The factor $\frac{1}{1 - \nu^2}$ originates from the fact that a tube is too rigid to bend longitudinally if subjected to a circumferential bending moment. This rigidity increases by the above fact as the stresses induced by a certain deflection compared with the stresses created by the same deflection in a narrow strip.

before (D_0) and after (D_1) splitting and $\Delta D_1 = D_1 - D_0$. The maximum stress (S_{\max}) is positive at the surface toward which the bending occurs.

Fundamentally, the same equation ap-

plicable manner by extending the simple splitting and slitting methods to samples from which successive surface layers have been removed by pickling (or machining). The total distribution can be derived from

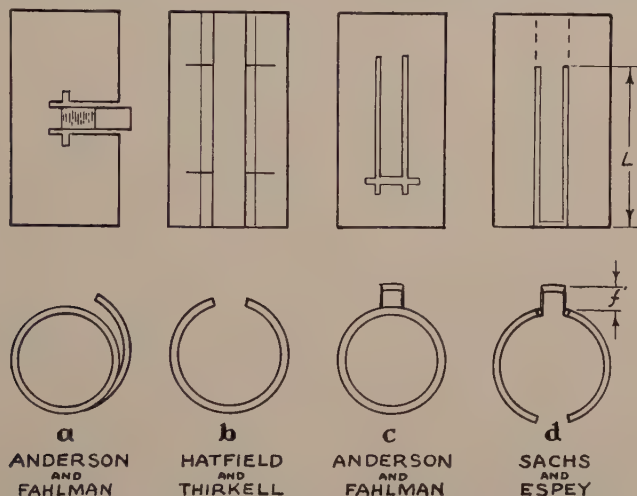


FIG. 1.—VARIOUS TESTING METHODS FOR MAGNITUDE OF RESIDUAL STRESS IN THIN-WALLED TUBING.

plies to the longitudinal stresses, which can be calculated from the deflection of a longitudinal tongue cut from the tubing (Figs. 1c and 1d).²⁻⁵

$$S = E(d - 2x) \frac{f''}{L^2} = E(d - 2x)f_1$$

where $f_1 = f''/L^2$ and f'' is the end deflection of the gauge length L .

If the residual stresses in a tube have an approximately linear distribution, these methods yield results that permit at least an approximate evaluation of the magnitude of the stresses. They have been used particularly for sunk tubing and drawn shells, but no attempts have been made to evaluate the applicability of these methods.

ACCURATE METHOD FOR DETERMINATION OF RESIDUAL STRESS DISTRIBUTION IN THIN-WALLED TUBING

The stress distribution in thin-walled tubing can be determined in a more quanti-

sets of experiments in which layers from either the outside or the inside are removed. The pickling can be done either before or after the splitting. In the latter case a single specimen may serve for each set of experiments, while the former procedure requires a separate specimen for each measurement, or an approximate total of 15 to 25 specimens. However, the uniform pickling of one surface of a sample already split is difficult.

Such a procedure has been suggested by Fox,⁷ who, however, did not succeed in developing a proper mathematical procedure. The theory of this method has been worked out by Dawidenkow⁸ but his set of formulas appear to be unnecessarily complicated, in consideration of the fact that certain arbitrary assumptions and resulting deviations are unavoidable.

Therefore, a comparatively simple set of equations has been worked out for calculating the circumferential and longitudinal stresses in tubing.

Circumferential Stresses

The following will be postulated: In Fig. 2 the thickness (x) removed, by pickling, from the original wall thickness d is positive in the direction of pickling. The change (ΔD) of the diameter D is positive if the specimen curves toward the direction

$\Delta D = \Delta D' - \Delta D_1$, where $\Delta D'$ is the diameter change after splitting and subsequent pickling:

$$S_3 = \frac{E}{1 - \nu^2} (d - x) \frac{\Delta D}{D_m^2}$$

Eventually, the removal of a layer (dx) (Fig. 2d) relieves the stress S_4 , still retained

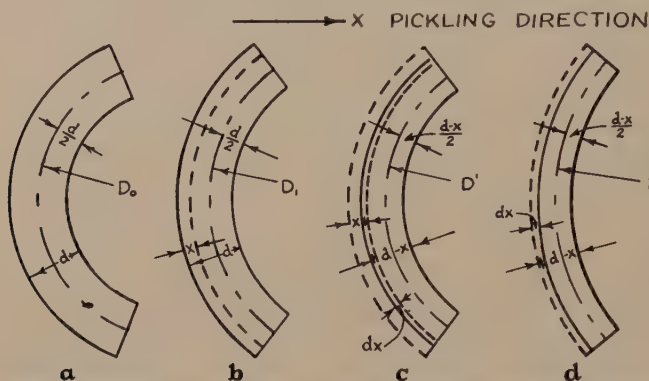


FIG. 2.—STEPWISE RELIEF OF COMPONENT STRESSES WITH SPLITTING AND PICKLING OF CIRCUMFERENTIAL SECTION.

of pickling (D increases in outside pickling, but decreases in inside pickling). The total stress in the fiber (x) may be considered as being relieved in three steps, yielding four stress components S_1 , S_2 , S_3 and S_4 .

The splitting operation relieves the previously derived stress component (Fig. 2b):

$$S_1 = \frac{E}{1 - \nu^2} (d - 2x) \frac{\Delta D_1}{D_m^2}$$

where D_m is now a mean diameter, which is selected according to the later discussed consideration S .

By removing a layer (x), two types of stresses are relieved. The component S_2 results from the release of the stresses in the removed layer (Fig. 2c):

$$S_2(d - x) + \int_0^x (S - S_1) \times dx = 0$$

$$S_2 = -\frac{1}{d - x} \times \int_0^x (S - S_1) \times dx$$

The component S_3 originates in the same operation from the release of the bending moment resulting in the diameter change

in this layer, causing a deflection, ΔD . This deflection results from the removal of the bending moment, dM , according to the general relations:

$$M = \frac{E}{1 - \nu^2} I \times \frac{2\Delta D}{D_m^2}$$

The moment of inertia of the strip of the thickness $d - x$ and unit width is $\frac{(d - x)^3}{12}$

$$\text{Therefore: } dM = \frac{E}{1 - \nu^2} \frac{(d - x)^3}{6} \times \frac{\Delta D}{D_m^2}$$

$$\text{and also, } dM = -S_4 \times dx \times \frac{(d - x)^2}{2}$$

$$\text{Therefore, } S_4 = -\frac{E}{1 - \nu^2} \frac{(d - x)^2}{3D_m^2} \times \frac{dD}{dx}$$

Thus, the total stress becomes:

$$\begin{aligned} S &= \frac{E}{1 - \nu^2} \times (d - 2x) \times \frac{\Delta D_1}{D_m^2} \\ &\quad + \frac{E}{1 - \nu^2} \times (d - x) \times \frac{\Delta D}{D_m^2} \\ &\quad - \frac{E}{1 - \nu^2} \times \frac{(d - x)^2}{3D_m^2} \times \frac{dD}{dx} \\ &\quad - \frac{1}{d - x} \int_0^x (S - S_1) \times dx \end{aligned}$$

The mean diameter D_m used in the foregoing equations varies considerably, depending upon the diameter changes

The deflections are positive if the tongue curves in the direction of pickling (+x), Fig. 3.

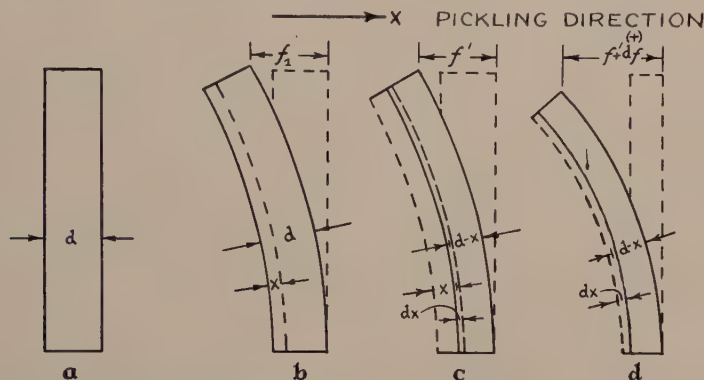


FIG. 3.—STEPWISE RELIEF OF COMPONENT STRESSES WITH SLITTING AND PICKLING OF LONGITUDINAL SECTION.

occurring and also upon the decrease in wall thickness during pickling. Usually a selected constant value of D , somewhere between the inside and the outside diameter of the tube, can be used without greatly impairing the accuracy of the results. This modification of the equations will be discussed in detail later, under the calculations.

Longitudinal Stresses

Fundamentally, the same derivation of formulas applies to the longitudinal stresses (Fig. 3) after replacing $E/1 - \nu^2$ by E , and $\frac{\Delta D}{D_m^2}$ by f .

This results in the final equation:

$$S = E(d - 2x)f_1 + E(d - x) \times f - \frac{E(d - x)^2}{3} \frac{df}{dx} - \frac{1}{d - x} \int_0^x (S - S_1) dx$$

Where: S = longitudinal stress at x ,
 x = amount of wall removed,
 f_1 = unit deflection after slitting,
 f' = unit deflection after slitting and subsequent pickling,
 $f = f' - f_1$,
 E = modulus of elasticity,
 d = original wall thickness,
 $S_1 = E(d - 2x)f_1$.

EXPERIMENTAL DETERMINATION OF RESIDUAL STRESSES

The theory developed for the calculation of the residual stresses involves a number of measurements, the results of which depend considerably upon the experimental technique. In order to obtain measurements sufficiently accurate for stress calculation and to evaluate the probable accuracy, a number of variable factors in the experimental technique were investigated and the procedures adopted accordingly.

THE SPLITTING OPERATION

Hatfield and Thirkell¹, also Anderson and Fahlman⁶, introduced as a testing method for the magnitude of circumferential stresses in thin-walled tubing the longitudinal slitting of a specimen, or slitting of a circumferential tongue (Figs. 1b, 1a). There does not appear to be any fundamental difference between the two methods, therefore the simpler method of splitting a standard length of tubing (2 to 3 diameters) was used.

The diameter change (opening or closing) of the tubing can be measured in the fol-

lowing manner: Two parallel lines, a suitable distance ($\frac{1}{8}$ in.) apart, are scribed longitudinally on the specimen by

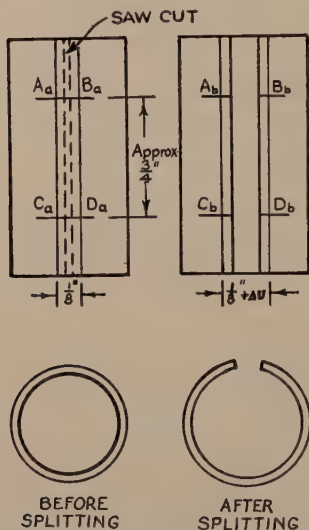


FIG. 4.—METHOD OF MEASURING CIRCUMFERENTIAL CHANGE OF TUBING ON SPLITTING.

means of dividers. Two lines perpendicular to and intersecting these longitudinal lines are scribed at points equidistant from both ends (Fig. 4).

The distances between the gauge points A, B, C, D , are measured before (A_aB_a, C_aD_a), and after (A_bB_b, C_bD_b) splitting, by means of a measuring microscope or comparator. The measurements are chords, therefore they must first be transformed into arcs, the correction usually being small. This yields the corrected values, $A'_aB'_a, C'_aD'_a, A'_bB'_b, C'_bD'_b$, which determine the change in circumference, U :

$$\Delta U = \frac{A'_bB'_b + C'_bD'_b - A'_aB'_a - C'_aD'_a}{2}$$

and, consequently, the change in diameter

$$\Delta D = D_1 - D_0 = \frac{\Delta U}{\pi}$$

The measured diameter change is affected by the type of tool used in splitting and the length of the specimen.

To determine the extent of these effects, two series of specimens were cut from a sunk cartridge-brass tube, varying the

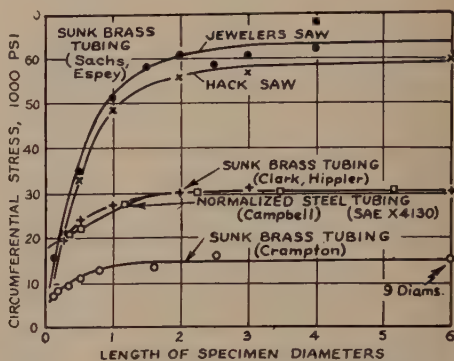


FIG. 5.—EFFECT OF SPECIMEN LENGTH ON RESIDUAL CIRCUMFERENTIAL STRESS IN TUBING, DETERMINED BY SPLITTING.

length from $\frac{1}{8}$ to 3 in., the two series differing in that one was cut and split with a hand hack saw and the other with a jeweler's saw (blade No. 1). The results (Fig. 5) show that the type of cutting has some effect, the diameter changes obtained using the jeweler's saw being, by a small constant value, higher than those obtained using the hack saw. This indicates that the cutting releases the stresses in a narrow strip of metal adjacent to the cut and that this loss can be minimized by the use of suitable tools.

According to Fig. 5, the measured diameter change depends upon the length of the specimen. This effect has been studied previously by Crampton,³ Clark and Hippler,⁹ and Sachs and Campbell,¹⁰ their results being shown in Fig. 5. (All work mentioned was done on sunk 70-30 brass except Sachs and Campbell's, which was done on normalized S.A.E. X 4130 steel tubing.) The figure indicates that with a length greater than 3 diameters the end effect becomes negligible because of the logarithmic trend of the curve. The shape of these curves can be explained by the release of longitudinal stress during the cut-

ting operation; however, the extent of such an effect cannot be evaluated at the present time. The stress relief presumably increases with the magnitude of the longi-



FIG. 6.—END DISTORTION ON SLITTING A LONGITUDINAL TONGUE WITHOUT RELIEVING CIRCUMFERENTIAL STRESS.

tudinal stresses, and extends to a depth proportional to the diameter of the tube.

CUTTING A LONGITUDINAL TONGUE

Anderson and Fahlman⁶ suggested, as a testing method for the magnitude of the longitudinal stresses in thin-walled tubing, the slitting of a narrow tongue from the specimen (Fig. 1c), this being accomplished in a milling machine. This operation is difficult to perform with small-diameter tubing, and a different procedure was adopted.

Attempts were made to slit the tongue from the specimens starting from one end. However, the slit end distorted (Fig. 6), owing to simultaneous release of longitudinal and circumferential stresses, and the measurements were difficult to make.

The procedure finally adopted consisted of slitting a tongue from specimens previously split longitudinally to release the circumferential stress (Fig. 1d). In this manner, one specimen can be used for both circumferential and longitudinal deflection measurements. Two additional parallel lines are scribed longitudinally on the specimens, approximately opposite the split, and used as a guide to saw a tongue (Fig. 1d). This operation causes the strip to deflect in the form of a circular arc.

This deflection can be evaluated by two procedures, either measuring the end deflection from its original position (Fig.

1d) or the center deflection (Fig. 7) from a given length (using a 1-in. knife edge as a base). It was found that the measurement of the end deflection, which is considerably

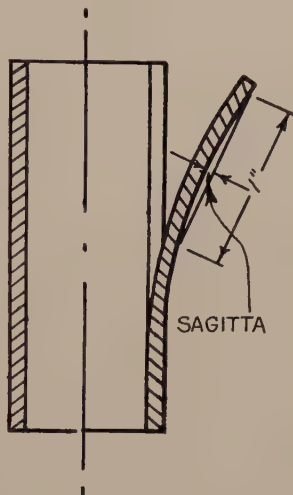


FIG. 7.—CENTER DEFLECTION OF ARC (SAGITTA).

larger than the center deflection (at least four times) yielded more accurate results. For this purpose the saw cut was made in such a manner that the base of the tongue was perpendicular to the tube axis, so that the length of the tongue could be accurately measured. The deflection was measured by means of a measuring microscope in the end plane perpendicular to the tube axis. From the measured values a constant correction distance had to be subtracted, as illustrated in Fig. 8. The deflections of a standard-gauge length of 1 in. were calculated from the corrected value (f''):

$$f_1 = f''/L^2$$

where L is the actual length of tongue.

The principal factor in the procedure that had a bearing on the measured deflections was the ratio of the width of the strip to the diameter of the tube (Fig. 9). This effect has been studied by Crampton,³ his results and those obtained in this investi-

gation agreeing closely. A maximum deflection was obtained when the width of the tongue was between 0.1 and 0.2 diameter. Narrower tongues deflect less,

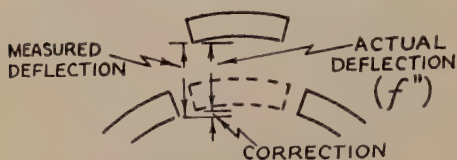


FIG. 8.—CORRECTION FOR MEASURED END DEFLECTION.

probably because of the elimination of stress by the cutting operation. Presumably the release of stress by slitting should extend to a distance proportional to the thickness of the tube. With increas-

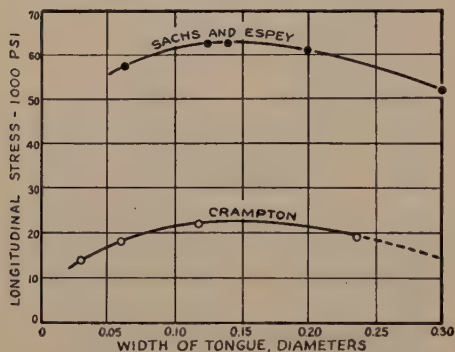


FIG. 9.—EFFECT OF TONGUE WIDTH ON RESIDUAL LONGITUDINAL STRESS IN SUNK BRASS TUBING, DETERMINED BY SLITTING TONGUE.

ing width of tongue, and after passing through the maximum, the deflection decreases very rapidly to small values because of the increasing curvature and stiffness of the tongue (section modulus). Owing to the combined action of the two effects, and adding a probable small effect of the saw cut itself, the measured deflections may be up to an estimated 10 per cent smaller than those expected for a tongue not subjected to such effects.

PICKLING

Two different sequences of operations can be followed to determine the stress distribution:

1. One specimen each is split and slit respectively and subjected to intermittent pickling of the one surface. After each pickling operation the wall thickness, the

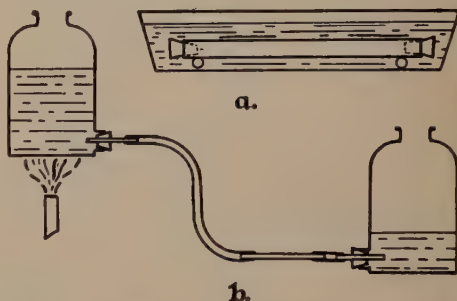


FIG. 10.—METHOD OF PICKLING: (A) OUTSIDE PICKLE; (B) INSIDE PICKLE.

change in diameter and the longitudinal deflection are measured.

2. A number of specimens are pickled to various wall thicknesses, each specimen is split longitudinally and the change in circumference is measured; a longitudinal tongue is then slit in the same specimen and its end deflection measured.

The result of the stress determination should be independent of the sequence of the slitting and pickling operation, this being a general rule for elastic stress conditions. However, no attempt has been made to confirm such an assumption as it was found difficult to pickle uniformly the split specimens. Therefore, separate specimens were used for each pickling operation. This also has the advantage that the final results represent the average condition over a considerable length of tubing.

It is not possible to make the necessary measurements accurately enough on tubing with a wall thickness below approximately 0.010 in. Therefore, in order to secure the total stress distribution, two series of specimens, pickled from the outside and inside respectively, must usually be investigated. This resulted in some overlapping, and therefore the mutual check of results.

The following procedure was adopted for pickling brass tubing of $\frac{1}{2}$ -in. diameter. For each set of measurements a piece of tubing about 3 ft. long was used. The

solution of nitric acid (1.42 sp. gr.) at 160° to 175°F . (70° to 80°C .) was used for the pickling, the concentrations being approximately maintained by adding concentrated

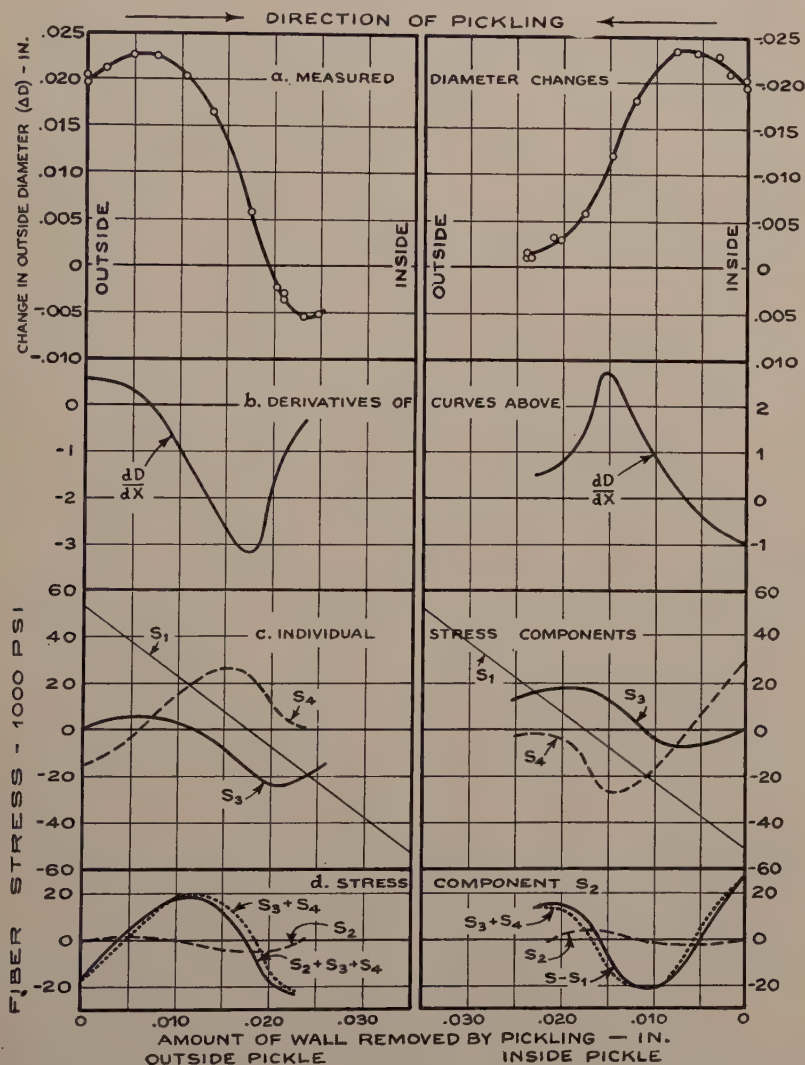


FIG. 11.—STEPS IN DETERMINATION OF STRESS DISTRIBUTION IN SUNK CARTRIDGE-BRASS TUBING.

residual stresses in at least three specimens, taken from both ends and the middle of the as-drawn tubing, were measured. The specimens were cleaned with carbon tetrachloride. A 20 per cent (by volume)

acid. The rate of pickling was found to be 0.0005 to 0.001 in. per minute. The apparatus used for the removal of the outside and inside of the tube by pickling is diagrammatically illustrated in Fig. 10a

and Fig. 10b, respectively. In order to pickle the outside (Fig. 10a), pieces 10 in. long were closed at the ends by means of rubber stoppers, immersed in the pickling

specimens cut from the ends, after the outside diameter had been measured in order to determine the amount removed. In order to pickle the inside (Fig. 10b), a

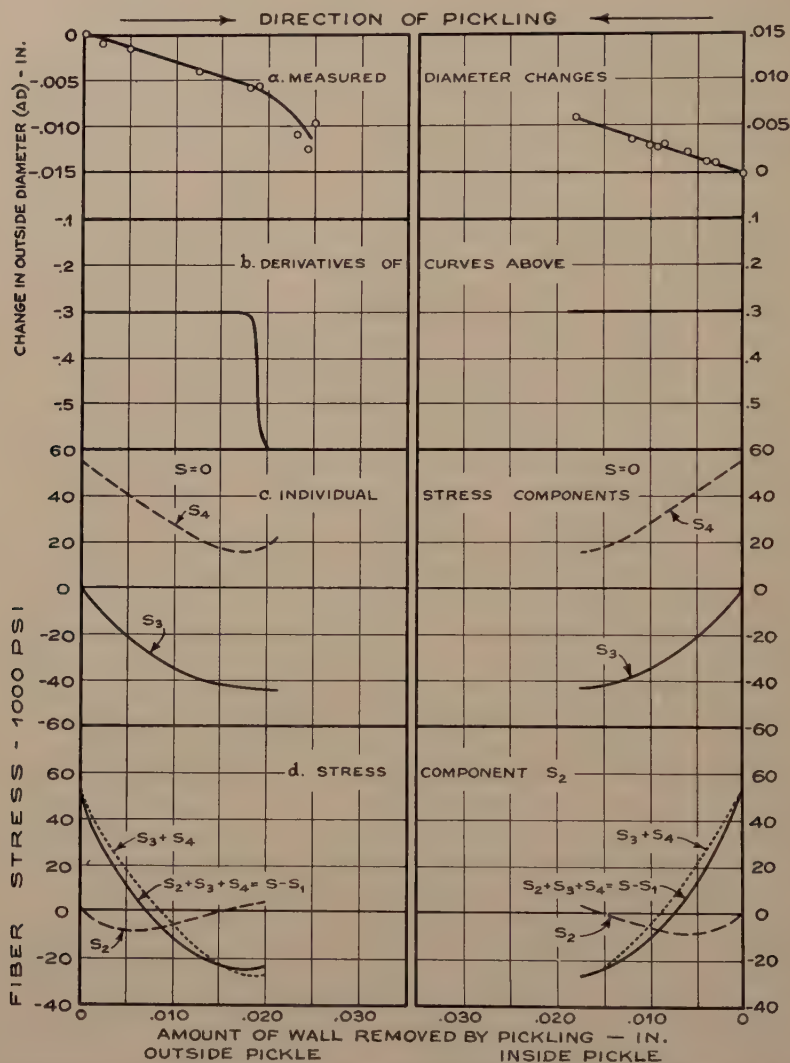


FIG. 12.—STEPS IN DETERMINATION OF STRESS DISTRIBUTION IN OIL-QUENCHED S.A.E.X-4130 TUBING.

tray and slowly rolled to secure uniform attack, being kept off the bottom by means of glass rods. At intervals, the tubing was washed in hot water and one or several

10-in. length of tubing was connected by rubber tubing with two bottles containing the hot acid. The bottles were alternately raised and lowered approximately $1\frac{1}{2}$ ft.

above or below the level of the solution in the other, thus causing a rapid flow of the hot solution through the tubing. Again, at intervals, the tubing was washed in hot water and one or several specimens cut from the ends. After the circumferential change and end deflection were measured, each specimen was cut into two pieces and the average wall thickness was determined. The wall thickness was found to be uniform within ± 0.0005 in. for the outside pickling and within ± 0.001 in. for the inside pickling.

PROCEDURE OF CALCULATION

The finally adopted procedure for computing the stress distribution may be illustrated for the examples, for a cartridge-brass tubing, sunk from $\frac{9}{16}$ in. outside diameter and $\frac{1}{32}$ in. wall thickness to $\frac{1}{2}$ in. outside diameter (Fig. 11) and an oil-quenched S.A.E. X 4130 steel tubing, $\frac{7}{8}$ in. outside diameter and $\frac{1}{32}$ in. wall thickness (Fig. 12). The computation consists of the following steps:

1. The measured circumference changes are converted into diameter changes (ΔD), which are plotted (Figs. 11a and 12a) against the amount x of wall removed. x is positive for outside pickling but negative for inside pickling.

2. From the carefully drawn trend curve ($\Delta D - x$) of each series, the derivative or slope (dD/dx) is determined graphically for various values of x in suitable steps, such as in steps of 0.0025 in. for the examples ($x = 0$, $x = 0.0025$, $x = 0.005 \dots$) up to the limit of possible accurate readings. In order further to improve the accuracy, the derived values of each series are plotted (Figs. 11b and 12b) against x and a trend curve ($dD/dx - x$) is drawn.

3. The trend curves permit calculation of S_1 , S_3 and S_4 for values of x in suitable steps (Figs. 11c and 12c).

4. Regarding the still unknown stress component S_2 , the formula:

$$S_2 = \frac{1}{d-x} \int_0^x (S - S_1) \times dx \\ = \frac{1}{d-x} \int_0^x (S_2 + S_3 + S_4) dx$$

contains the term $\int_0^x (S_2 + S_3 + S_4) dx$ which constitutes the area:

$$A = \int_0^x dA$$

between the x axis and the curve $(S_2 + S_3 + S_4)$ above the length x . This area is

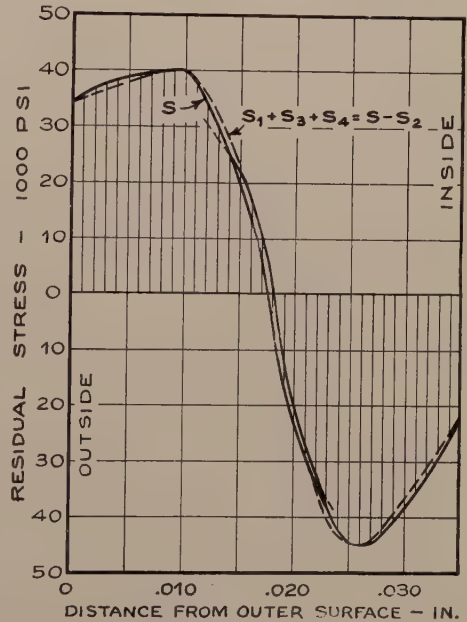


FIG. 13.—DISTRIBUTION OF RESIDUAL CIRCUMFERENTIAL STRESS IN BRASS TUBING 0.500 INCH OUTSIDE DIAMETER, 0.0345 INCH WALL THICKNESS, SUNK FROM 0.625 INCH OUTSIDE DIAMETER THROUGH A 12.5° HALF-ANGLE CHROMIUM-PLATED DIE.

only slightly smaller than that formed by the known values $(S_3 + S_4)$, and it is possible to estimate S_2 by extrapolation sufficiently close for the integration, yielding the accurate value of S_2 :

$$S_2 = \frac{A}{d-x}$$

In carrying out this computation, it has been found that S_2 becomes rather small if the stress component S_1 is large, as for the sunk brass tubing (Fig. 11d, e and f).

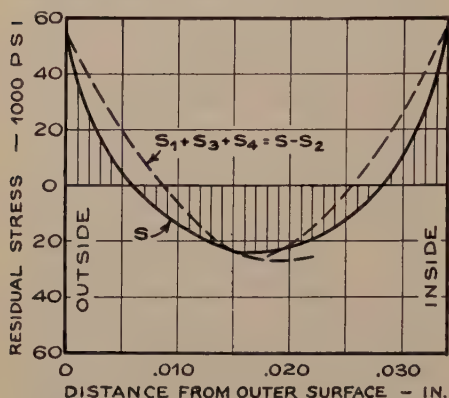


FIG. 14.—DISTRIBUTION OF RESIDUAL CIRCUMFERENTIAL STRESS IN S.A.E. X-4130 TUBING, 0.875 INCH OUTSIDE DIAMETER, 0.034 INCH WALL THICKNESS, OIL-QUENCHED FROM 1550°F.

S_2 can be neglected in such cases, as it affects only slightly the final stress distribution (Fig. 13). If, however, S_1 is small, S_2 becomes significant and is of considerable influence, regarding the final stress distribution (Fig. 14).

The derived equations would be correct for tubing with an infinitely thin wall, but they become less accurate for increasing wall thickness. While it may be concluded that even for tubing of substantial wall thickness the equations may serve as a first approximation, the uncertainty also includes the use of the equation itself. The two terms ΔD and D_m are not completely defined, and it has been found that D may be generally taken as the change of the outside diameter. On the other hand, the "mean" diameter D_m has thereby introduced errors ranging within reasonable limits, say ± 10 per cent. Thus, it has been found that in the case of the brass tubing the mean diameter may be taken as the outside diameter minus one half the wall thickness, while in the case of the steel tubing the mean diameter of the unsplit tubing already yields the desired accuracy.

Such a simplification will be permissible in the majority of applications.

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DISCUSSION

(S. L. Hoyt presiding)

T. A. READ,* Philadelphia, Pa.—A comparison of your formulas for the determination of the stresses in tubing with those of Dawidenkow shows that the two expressions for the contribution S_4 are identical, and that the two expressions for S_1 differ only in that Dawidenkow took into account the separation between the neutral axis and the center of the wall. On the other hand, Dawidenkow's expressions for S_2 and S_3 are not the same as yours. Will you please indicate the significance of this difference?

G. SACHS.—It is difficult to compare the equations derived by Dawidenkow and the authors. Both sets contain integrals but the variables are different. There is no exact solution possible for the equation presented by the authors, as the component S_2 involves a mathematical series. It should be possible to transform the one form into the other equation. This, however, appears to involve tedious calculations, which have not been carried through.

T. A. READ.—Have you made calculations from the same formula using Dawidenkow's formula?

G. SACHS.—No, we have not. However, we have in reality checked ourselves because the results of pickling from both the inside and the outside agree in the center, where they

* Ordnance Laboratory, Frankford Arsenal.

overlap, and the tension and compression areas are equal. This would indicate that the formulas are substantially correct.

A. V. DEFOREST,* Cambridge, Mass.—Might I ask whether the pickling off method of removing the surface layers gives approximately the same result that grinding off would give, so as to check whether or not the pickling changes the stress distribution below the surface that is actually removed by the acid?

G. SACHS.—Of course there is grinding, where the surface of the metal may be flowed and tempered, and careful grinding where the results may be as good as obtained in controlled machining. This may be applied to pickling to a minor extent.

A. V. DEFOREST.—Both the etching and the grinding and the machining depend on the supposition that the surface is left free of stress at the point at which the metal is removed. I should think it would be quite a problem to estimate whether that were true or not in the case of the pickling, especially where the metal is being removed on a side that has residual tension.

G. SACHS.—So far, the pickling appears to be the cleanest procedure of these three. Pickling, as we know from electrolytic polishing, does not distort the surface layers of the metal. In grinding or machining, however, the surface layers are deformed considerably.

A. V. DEFOREST.—There is pickling and pickling. This is good pickling. There is the same difficulty involved in a chemical attack that there is in the grinding and the machining. It must be done right.

G. SACHS.—It is difficult to imagine that pickling should attack layers of metal three or four thousandths of an inch below the surface. This is not only possible but definitely the case with machining. The effects of machining go as deep as four or five thousandths or even more.

A. V. DEFOREST.—Pickling can go deeper than that when it attacks the grain boundaries of material under tension.

S. L. HOYT,† Columbus, Ohio.—Dr. Sachs, it seems to me that that is an important point.

Would you describe that detail of your work a little bit more carefully—the kind of acid that you use, and so forth?

G. SACHS.—One requirement for good pickling is that a uniform wall decrease shall be obtained as well as little grain-boundary attack. The check of the stress distributions for both the inside and the outside pickling, I believe, prove that our pickling was in order.

A. V. DEFOREST.—That is pretty good proof that the pickling used was good.

MEMBER.—What is the possible effect of absorption of hydrogen in pickling? Often there is a possibility of introducing stress in pickling steels if hydrogen is absorbed.

G. SACHS.—Any effect of this type has a meaning only if it is deep enough. We remove layers in steps of a couple of thousandths, and any distortion that does not go deeper than a few tens of thousandths has no quantitative effect on the results. It must go a thousandth or so deep to show up in the results at all.

R. M. BOZORTH,* New York, N. Y.—I do not believe you could get hydrogen with nitric acid, could you?

G. SACHS.—I do not think so.

R. H. HEYER,† Middletown, Ohio.—It would seem as though this were an ideal application for anodic electrolytic pickling that would remove metal without hydrogen pickup.

G. SACHS.—I will report tomorrow on some surface effects (see p. 67). Our factor of uncertainty is high because we are talking about layers of one or two thousandths thickness, and anything that interferes from the outside may have a considerable bearing on the results.

C. W. MACGREGOR,‡ Cambridge, Mass.—Referring to Figs. 13 and 14, what is the sign of the stresses plotted about the horizontal axes?

G. SACHS.—They are positive.

S. L. HOYT.—Mr. Templin, how would you etch aluminum tubes to carry out this procedure?

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‡ Associate Professor, Applied Mechanics, Massachusetts Institute of Technology.

* Professor of Mechanical Engineering, Massachusetts Institute of Technology.

† Technical Adviser, Battelle Memorial Institute.

R. L. TEMPLIN,* New Kensington, Pa.—In such work as we have done along this line we have preferred the machining operations to get at the measuring of such stresses as are mentioned here. We do not know how accurate the work is, but at least it serves a very useful purpose to us and we think the results, qualitatively at least, are rather significant. Quantitatively, I do not know to what extent we would want to depend on it.

G. SACHS.—We estimate the stress to be accurate within minus zero and plus 30 per cent. The probability is that the stresses are considerably underestimated. That means a ± 15 per cent scattering, with the probability that the actual stress is 15 per cent higher than the calculated values.

S. L. HOYT.—You have described a method of determining stresses that involves slitting a sample, and a second one of etching off layers. How would you compare those two methods for application, and so forth? Do you use both, or have you a preference?

G. SACHS.—For the example in Fig. 13, the approximate stress (S_1) was 53,000 lb. per sq. in. at the surface while 35,000 lb. per sq. in. was the stress at the surface according to our equation, and 40,000 lb. per sq. in. was the highest stress in the section. Here the approximation method gives 50 and 30 per cent, respectively, higher values than the accurate method.

For the example in Fig. 14, the approximation method gave zero stress while the accurate method gave stresses varying from 50,000 lb. per sq. in. at the surface to 25,000 compression at the center of the section.

V. N. KRIVOBOK,† Burbank, Calif.—On normalized X4130 tubing—that seems to be a rather important product these days—locked-in internal stresses seem to be blamed for all sorts of troubles that are experienced with this particular steel. May I inquire if in your work you have attempted to stress the effect of drawing, both as to time and temperature, on the normalized tubing, and if so to what degree the tension and compression properties

have been affected by time-temperature treatment?

G. SACHS.—We published a short paper this month in the *Welding Journal* that gives the answer. Up to about 800°F. there is little influence, and then the stresses are removed fast, and become almost zero at an annealing temperature close to the critical.

V. N. KRIVOBOK.—I remember that paper with a great deal of interest. The time element has not been carried on far enough, as I recollect it.

G. SACHS.—That is correct, but usually we figure that doubling the time is equivalent to increasing the temperature by 20°F. This is just a rule of thumb, but one that works out fairly well. Most effects are of the diffusion type. If the temperature is reduced by 100°F. the time must be increased by 32 times to get the same effect; $\frac{1}{2}$ hr. at 900°F. is equivalent to 16 hr. at 800°F.

V. N. KRIVOBOK.—According to that work of yours, Dr. Sachs, the drawing at any temperature below 900°F., if I recollect the figures correctly, should have no effect at all on the, shall we say, relief of stresses.

G. SACHS.—Not within a short time of annealing.

V. N. KRIVOBOK.—In other words, according to the work you have done you can relieve stresses or temperatures below 900°F.?

G. SACHS.—Yes.

V. N. KRIVOBOK.—At the morning session today in the American Welding Society program a statement was made that no relief of stress could be accomplished at temperatures below 1200°F.

I am glad to learn you agree with me. All that is necessary is to increase the time and thereby relieve some of the stresses. Is that correct?

G. SACHS.—That is correct. I know, of course, that the present-day practice is to stress relief, or to treat it at 1100°, is that right?

V. N. KRIVOBOK.—That is right.

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† Director of Research, Lockheed Aircraft Corporation.

Theory of Lattice Expansion Introduced by Cold-work

BY CLARENCE ZENER,* JUNIOR MEMBER A.I.M.E.

(Philadelphia Meeting, October 1941)

GENERAL THEORY

It has long been known that the density of a metal usually decreases with cold-work. Thus O'Neill¹ observed as early as 1861 that cold hammering of commercial hot-rolled copper is accompanied by a decrease of density of 0.2 per cent, and that subsequent annealing restores the original density. The origin of this density change, however, has remained obscure. In particular, experiment has not yet decided whether it is due to the presence of small cavities and an increase in intergranular surface or to an actual expansion of the lattice itself.

This uncertainty in the origin of the change in density is a reflection of our uncertainty as to the changes induced in a metal by cold-working. One school regards cold-working as a breaking up of the original grains into a large number of perfect crystallites somewhat randomly orientated with respect to one another.² According to this viewpoint, the mere introduction of a large intercrystallite surface induces a net volume expansion. Another school regards cold-working primarily as a distortion of the grains. It is not obvious that this second viewpoint will lead to a net volume expansion. The purpose of the present paper is to show that this is indeed the case, and that this

expansion is of the right order of magnitude to explain existing experimental data.

The physical basis for the association of an expansion with distortion lies essentially in the variation of the elastic moduli with volume. This variation is considerable. Thus from Table I we see that a 1 per cent increase in volume for the case of copper will decrease the bulk modulus K by 10 per cent, the shearing modulus μ by 3.8 per cent. If we thus twist a rod through a given angle, we shall do less work upon it if it increases slightly in volume, thereby reducing the torsion modulus that involves as a factor the shearing modulus. A general principle³ in physics states that the rod will so adjust itself as to have a minimum potential energy consistent with the end restraints. It will therefore expand.

TABLE I.—*Dependence of Elastic Moduli upon Dilatation*^b

Metal	$-d \ln K / d \ln V$	$-d \ln \mu / d \ln V$
Aluminum.....	3.3 ^a	5.7
Copper.....	10.0	3.8
Iron.....	7.5 ^a	3.7

^a Measurements on single crystals, all others on polycrystalline rods.

In order to obtain a quantitative comparison with experiment, we follow Maier⁴ in comparing the lattice expansion with the latent energy of cold-work. This latent energy has been measured directly by Taylor and Quinney⁵ on copper rods subjected to torsion, and may amount to as much as 15 per cent of the total work done upon the specimens. We shall assume that this

Manuscript received at the office of the Institute July 25, 1941. Issued as T.P. 1403 in METALS TECHNOLOGY, December 1941.

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¹ References are at the end of the paper.

latent energy resides primarily in lattice distortions, that only a negligible part is associated with new grain boundaries. The fact that these distortions have actually been produced irreversibly in no wise prevents us from analyzing them by a thermodynamic method; for a fair approximation to the final cold-worked state may be arrived at in a reversible manner, at least in thought. This may be done as follows. We imagine certain internal areas in the metal to be temporarily relieved of all shearing strength. We may then allow slip to occur reversibly across these areas, and only then restore their original shearing strength.

TABLE 2.—*Ratio of Net Dilatation to Latent Energy of Cold-work*
CUBIC CENTIMETERS PER ERG

Metal	Pure Microscopic Dilatations	Pure Microscopic Shears
Aluminum.....	3.2×10^{-12}	6.5×10^{-12}
Copper.....	7.3	2.3
Iron.....	3.9	1.6

Our problem is now fairly definite. We suppose the solid to contain internal stresses. These will be taken as completely arbitrary, save for the conditions that they form a self-equilibrating system, and that their tractions vanish across all exterior surfaces. We are to find the relation between the net expansion and the latent energy associated with these stresses. Unfortunately, this problem may not be solved uniquely. For the latent energy exists in two forms, as energy of dilatation and as energy of shear. At present there is no way of determining how the energy is distributed into these two types of distortion. In the next section we shall calculate the net dilatation due to unit energy per unit volume stored in microscopic pure dilatation, and also the net dilatation due to unit energy per unit volume stored in a distribution of pure shearing stresses. It is to be expected that the actual value will

lie between these two extreme values. These dilatations are given by Eqs. 6 and 8, respectively. From these equations we construct Table 2, using the derivatives in Table 1, and taking the bulk modulus K for aluminum, copper and iron⁷ as 0.73, 1.24, 1.67×10^{12} erg per c.c., respectively.

By comparing his observations on the variation of density with cold-work with the observations of Taylor and Quinney⁸ on the variation of the latent energy with the same type of cold-work, Maier⁴ has obtained, for copper, an estimate of the variation of density with the latent energy of cold-work. He found that for samples with small grain size the density increased with the amount of cold-work, while for specimens with large grain size the density decreased. We shall compare our calculations with the experiments on large-grain-size specimens where the disturbing effects of grain boundaries are a minimum. From Maier's data (his Fig. 9) we obtain, for the large-grain-size specimens, 2.7×10^{-12} c.c. per erg as the ratio of dilatation to latent energy of cold-work. This ratio lies between the two extreme theoretical values for copper in Table 2. We conclude that Maier's observations are consistent with the viewpoint that all the latent energy of cold-work goes into distortion of the lattice.

This conclusion is diametrically opposed to that of Maier. By a supposedly rigorous thermodynamical analysis of his own data, he proved that the dilatation of the large-grain-sized copper specimens would be of the order of 10 times that observed if all the latent energy of cold-work went into lattice distortion. Maier's error arose from his failure to inject any physics into his argument. Thus the only strain allowed by his analysis was a dilatation uniform throughout the entire specimen, which would of course be unstable without the application of a negative pressure. The latent energy of distortion that he calculates (his Eq. 7) is simply the influx of heat that would accompany the application of

such a negative pressure, the work done by the negative pressure being a second-order small quantity. The change of heat content, ΔH , which he calculates (his Eq. 9) is devoid of any simple physical significance. For ΔH represents heat influx only for processes in which the pressure is maintained constant.

CALCULATIONS

Hooke's law, that strain is proportional to stress, is taken as fundamental to most problems in elasticity. According to this law, the dilatation Θ is given by

$$\Theta = (\sigma_x + \sigma_y + \sigma_z)/3K \quad [1]$$

Here K is the bulk modulus, and σ_x is the tensile stress across a plane normal to the x axis, while σ_y and σ_z have similar interpretations. If the specimen is subject to no external forces, the surface average of σ_x must be zero over all planes normal to the x axis; hence the volume average of σ_x must be zero over the entire specimen. Applying the same reasoning to σ_y and to σ_z we see that the average of Θ throughout the specimen must be zero, to the approximation of Hooke's law.

In order to obtain a nonvanishing value for the average of Θ , we must go beyond Hooke's law and add to the right member of Eq. 1 a second-order polynomial in the stresses. Fortunately, the choice of such a polynomial is severely limited by the principle of invariance. Thus Θ , a scalar, is invariant with respect to a rotation of coordinate axes. Hence the terms which we add to Eq. 1 must possess the same invariance. Only two linearly independent second-order polynomials are so invariant.⁸ They may be chosen as the work, per unit volume, done in establishing the dilatation and the shearing strains, respectively. We therefore have

$$(\Theta)_{\text{avo}} = C_d W_d + C_s W_s \quad [2]$$

where W_d and W_s represent the average work done upon unit volume of specimen

in establishing the microscopic dilatations and the shearing strains, respectively, and C_d and C_s are at present unknown multiplicative constants.

The constant C_d will first be calculated. In order to do this, we consider an elementary region of the specimen. Its volume before and after distortion will be denoted by v_i and v_f , respectively. The change in its volume, dv , associated with a change in pressure dp , is given by

$$dv/v = -dp/K(p). \quad [3]$$

In order to take explicit account of the variation of the bulk modulus K with pressure, we expand

$$1/K = 1/K_0 - (dK/dp)p/K_0^2 + \dots$$

Here K_0 denotes the bulk modulus at zero pressure. Upon substituting this expansion into Eq. 3, and integrating, we obtain

$$\ln(v_f/v_i) = -p/K_0 + (dK/dp)p^2/2K_0^2 + \dots \quad [4]$$

In averaging $\Delta v = v_f - v_i$ over the specimen, care must be taken to let the element of volume refer explicitly either to an element of the undistorted specimen or to an element of the distorted specimen. The answer will be the same in either case, but the details of the calculation will be different. We shall use the latter interpretation of the element of volume, since in this case the integral of $p = -(\sigma_x + \sigma_y + \sigma_z)/3$ over the specimen vanishes. It is then necessary to expand $\ln(v_f/v_i)$ in the series

$$\Delta v/v_f + \frac{1}{2}(\Delta v/v_f)^2 + \dots$$

Upon substituting this expansion into Eq. 4, and neglecting powers of small-order quantities greater than the second, we obtain

$$\Delta v = \{-p/K_0 - \frac{1}{2}(\Delta v/v_f)^2 + (dK/dp)p^2/2K_0^2\} \cdot v_f.$$

We now sum this equation over all the elementary volumes v_f , and then divide

by the total volume of the specimen. In the right-hand member, the first term vanishes, as has previously been mentioned. In the second term $(\Delta v/v)^2$ differs from $(\Delta v/v_s)^2$ by a small quantity of a higher order than the second. It may hence be replaced by Θ^2 . Finally, in the third term $(p/K_0)^2$ may also be replaced by Θ^2 . We thus obtain for that part of the net dilatation due to microscopic dilatations

$$(\Theta)_{\text{ave}} = \frac{1}{2}\{-1 + dK/dp\}(\Theta^2)_{\text{ave}} \quad [5]$$

In order to emphasize the dimensionless nature of dK/dp , we write it in the form $-d \ln K/d \ln V$. Since $W_d = \frac{1}{2}K(\Theta^2)_{\text{ave}}$, we have, upon comparison of Eqs. 2 and 5,

$$C_d = -(1 + d \ln K/d \ln V)/K \quad [6]$$

We next find the average dilatation due to the shearing stresses. We again consider an element of the specimen of such small volume v that the stresses therein may be regarded as uniform. The stress is to be such that the pressure p will be zero. The parameter α will be taken as a measure of the strain. The change in volume Δv of the element will be a quadratic function of α ,

$$\Delta v = \frac{1}{2}(\partial^2 v/\partial \alpha^2)\alpha^2 \quad [7]$$

Corresponding to the experimental condition that the volume after distortion be compared to the volume before distortion at the same temperature, the above derivative is to be calculated for both constant p and constant T . This may be done by the standard methods of thermodynamics. We take as independent variables T , p , α . Then the differential of the function $(E - TS + pv)$,

$$-S dT + v dp + A d\alpha$$

is a perfect differential. As is usual, E refers to the total energy content, S to the entropy. The force function A is so defined that $A d\alpha$ is the work done by the external forces when α changes by the amount $d\alpha$.

From the condition for a perfect differential we obtain

$$\partial v/\partial \alpha = \partial A/\partial p$$

Differentiating each side with respect to α , we obtain

$$\partial^2 v/\partial \alpha^2 = (\partial/\partial p)(\partial A/\partial \alpha)$$

Substitution of this into Eq. 7 gives

$$\Delta v = \{\partial \ln (\partial A/\partial \alpha)/\partial p\} \times \{\frac{1}{2}(\partial A/\partial \alpha)\alpha^2\}$$

Now $\partial A/\partial \alpha$ must be of the form $C\mu v$, where C is a constant and μ is the shear modulus. The first factor in the above equation therefore is $-1/K + \partial \ln \mu/\partial p$. The second factor is the work done by the force A . We thus obtain the second constant in Eq. 2,

$$C_s = -(1 + d \ln \mu/d \ln V)K^{-1} \quad [8]$$

Strictly, Eqs. 5 and 8 relate the net dilatation to the reversible work done upon the lattice in producing distortions. The energy associated with the distortion is this work plus the heat absorbed when the distortion is introduced isothermally. Calculation shows this latter to be quite small compared with the work, and so will be neglected.

SUMMARY

It is found that the volume of a metal free of external forces is greater when internal stresses are present than when they are absent. The increase in volume is proportional to the energy associated with these internal stresses. A quantitative calculation shows that this dilatation is of the right order of magnitude to account for the observed decrease in density of metals upon being cold-worked.

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DISCUSSION

(R. M. Bozorth presiding)

R. M. BOZORTH,* New York, N. Y.—As I understand it, this theory is based on the fact that there is a change in Young's modulus, or the other moduli, with expansion. I believe that is the fundamental assumption involved. This is a second order of approximation to Hooke's law, which Dr. Zener treated mathematically. Apparently, the result is quite consistent with the data.

It seems to me that it does not rule out another explanation, which is that cold-working will cause small dispersions to arise—holes in the lattice, we may say, or between grains—we will not specify how, and that these will also give rise to a decrease in density with cold-work.

I would like to ask Professor Nielsen if he thinks that other picture has been ruled out, or if this is just one possible theory?

H. NIELSEN,† Pullman, Wash.—No, it does not rule out that picture of mosaic structure, or whatever you want to call it—but the mosaic-structure idea is not necessary, of course, to this analysis.

G. SACHS,‡ Cleveland, Ohio.—Am I right that the assumption is that, in large-grained material, the density changes would be mostly caused by stress proper, while in fine-grained material the density decrease would be mostly caused by imperfections or holes between the grains and perhaps in the grains?

That agrees to a certain extent with other findings. We made some measurements of densities some years ago and found very small changes in single crystals. Somewhat higher decreases in density occurred when the slip mechanism in the single crystals became complex.

H. NIELSEN.—I do not believe that Dr. Zener has done any work on fine-grained material as yet. He did not commit himself. I do not know whether he is contemplating that or not.

L. PESSEL,§ Philadelphia, Pa.—Do you think there is any connection between this

phenomenon and the cold sintering of metal powders under pressure, which could be explained, at least partly, by lattice expansion?

H. NIELSEN.—I am not sure. I think that most powders would be a finer grain than the copper assumed here. So I do not suppose it would be directly applicable to that. I do not know, however. Does anybody else have any ideas about that?

W. E. KINGSTON,* Emporium, Pa.—In the process of drawing tungsten wire, after the powdered metal has been sintered to a maximum density of around 19.3 and subsequently drawn into fine wire, it is evident that the density does decrease slightly as the wire is drawn down during further cold-working. Using high magnifications, it is believed that the grains are so deformed that there are spaces or voids between the elongated grains, thus accounting for the reduction in density. This particular presentation would tend to indicate that the reduction in density is not due primarily to the condition first described, but rather to dilatation of the grains themselves.

H. NIELSEN.—It does not indicate necessarily that it is not true but that it is not necessary to explain the expansion.

W. E. KINGSTON.—Possibly both effects are present.

R. M. BOZORTH.—Perhaps the order of the magnitude of the effect would show the difference. That is, if these holes can be seen under the microscope, it may mean that the change might be larger than is accounted for on this theory. Have you any information on that?

H. NIELSEN.—I do not know.

W. E. KINGSTON.—The same is true of copper, nickel and other metals and alloys when reduced by cold-working to fine diameters, not only with sintered powdered metals but also metals and alloys made by normal casting methods.

M. AVRAMI,† New York, N. Y.—Dr. Nielsen has said twice that it does not matter whether or not the mosaic picture is accepted along with this analysis. I would like to ask him to be

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sure to make that clear; that is: there *could* be the change in mosaic structure, or the increased spacing between the particles, as the physical situation corresponding to the mathematically calculated lattice expansion. In other words, this is a formal theory, based upon classical elastic and thermodynamic considerations. It does not discuss the question as to whether the expansion takes place between the atoms in a single crystal or between the single crystals themselves. It merely says that in order to have equilibrium upon distortion, there must be a lattice expansion of volume. That can be either separation between the grains or separation of the atoms. It is not necessary that it be one or the other.

H. NIELSEN.—That is true; the expansion could be due to some sort of mosaic structure. But Zener is using the ordinary accepted formulas of elastic strain here in deriving his formula, so that it is certainly not necessary to accept the mosaic structure.

R. M. BOZORTH.—For example, the difference might be that Zener assumes implicitly that the strain is more or less uniform and if there were spaces between grains that would be just a nonuniform distribution of strains with a certain average value?

H. NIELSEN.—Yes, that is right.

H. H. LESTER,* Watertown, Mass.—The author has attacked a problem that is quite pertinent to national defense, inasmuch as cannon are at present cold-worked in manufacture. Perhaps some mention could have been made of the concept of the crystal as a geometric space pattern defining stable equilibrium in the system of atoms composing it. According to this concept, the spatial arrangements are those consistent with minimum potential energy, and any other arrangement, even one involving the displacement of only a single atom from its lattice point position, would increase that energy. It is to be expected that such an arrangement would be one of closest atom packing permitted under a given set of physical conditions, including temperature and pressure. If it is true that the geometrical condition for stable equilibrium is that of closest atomic packing, it follows that a dis-

tortion of the space pattern necessarily involves a packing that departs from the closest possible and hence a lowered density.

It is well known that plastically deformed metal contains residual elastic strains, which persist after the removal of the deforming load and disappear only upon the application of heat. Observed changes in density after cold-work could be the result of the presence of such strains. The present paper would seem to offer support to such a concept.

C. H. MATHEWSON,* New Haven, Conn.—No proved mechanism or generally accepted theory of crystal plasticity and strain-hardening of metals exists at the present time. This means that an essential element in the consideration of property changes customarily brought about in the working and heat-treatment of alloys cannot be critically evaluated. Nothing in the whole field of physical metallurgy is of greater fundamental importance than the interpretation of stress-strain relationships, with particular reference to the quantitative adjustment of atoms in groups, blocks, domains, crystallites, etc., following any disruptive process imposed upon the perfect crystal.

The author makes a definite contribution to this subject by demonstrating that the mathematical theory of elasticity can be used to predict a dilation defining a condition of internal stress, and therefore of strain energy, that is compatible with the observed (slight) decrease in density produced by cold-working. In reflecting upon this condition, which must be a product of slip in some adequate sense, one instinctively seeks to picture the process in simple mechanical terms, as indeed the very designation, slip, and the appearance of macroscopic slip bands demands. I have in many private communications and in a very brief description utilized by R. M. Brick and Arthur Phillips in a yearly review of physical metallurgy (MINING AND METALLURGY, February 1941) urged consideration of a possible form of slip in which at a certain critical value of stress (yield point) elastic shear strain in a large number of spacings (summation of many small shear strains) constituting paired blocks along the length of the axially strained crystal, forces plastic shear,

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* Professor of Metallurgy, Yale University.

viz., shear through one or more identity periods, in the boundary spacing shared by the two blocks. A precise analysis of such a process is difficult because: (1) the elastic shear strain utilized in the process cannot be quantitatively considered independently of other strain components associated with the axial tension stress, and (2) proportionality between stress and strain is not even approximately realized in the case of the large shear (slip) constituting a full movement through the identity period at the intermediate spacing between blocks.

However, at the conclusion of the process, a residual elastic shear strain in the intermediate spacing must be balanced against a residual elastic shear strain of opposite sign in the block spacings and it is now suggested that this model be regarded as a possible self-equilibrating system of internal stress, fulfilling the arbitrary condition defined by the author in stating the premises from which the mathematical development proceeds.

Another point of consequence may be made concerning the physical basis for lattice expansion in shear-strained metal, if we consider that a close-packed structure opposes shearing displacement of its interlocked planes. In order to accomplish slip in such a structure built with hard spheres, separation of the planes or a wholly fantastic interdeformation of the spheres would be necessary. A high degree of caution is advisable in pursuing such analogies, in the consideration of atomic phenomena, but the great resistance of metal lattices to volume compression gives effect to the conception that slip must be facilitated by dilation and that in consequence a system of balanced internal shear strains must be characterized by a net decrease in density, quite in conformity with the author's analytical conclusion.

In further pursuit of a useful analogy, it may be recalled that the direction of easy mechanical movement against one another of "nested" close-packed spheres assembled in planes of the form $\{111\}$ in the face-centered-cubic lattice, is $[11\bar{2}]$, the twinning movement, and not $[110]$, the slip movement. Slip through a full identity period may be differentiated into two separate $[11\bar{2}]$ movements, the first establishing a twin configuration at the affected spacing and the latter, a return to the original configuration. Thus, minute nuclei

for the growth of the familiar annealing twins may originate in a train of movements at block boundaries, operated by the action of the elastic shearing force in the blocks. This

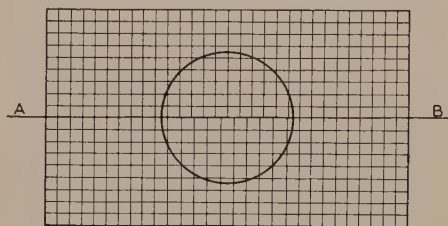


FIG. 1.

mechanism avoids the development of mechanical twinning as a mass effect and therefore is compatible with the difficult or uncertain experimental verification of the actual existence of twin elements in cold-worked face-centered-cubic metals prior to annealing.

F. SEITZ,* Philadelphia, Pa.—Professor Zener's interesting paper on the source of the lattice expansion produced by cold-work is particularly noteworthy because his results are independent of the atomic picture used to explain the distortion. It is interesting to observe, however, that the origin of the distortion may be pictured readily on the basis of the theory of dislocations. According to this picture, plastic flow in crystalline materials ordinarily occurs as the result of the production and motion of the type of lattice imperfection shown in Fig. 1, which is known as a *dislocation*. It may be shown⁹ that the motion of the center of this distortion can be produced by stresses of the order of magnitude of the observed critical shearing stresses of well-annealed metals, and that this motion results in "slip" or "translation" of one crystallographic plane relative to another. It may be noted that the part of the lattice immediately above the center of the dislocation is compressed, whereas that below is extended. It is a well-known fact that atoms resist compression more strongly than extension. This is made evident, for example, by the fact that the compressibility of crystals generally decrease with increasing pressure. As a result of this effect, the increase

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⁹ See, for the example, *The Journal of Applied Physics* (1941) **12**, 100, 170, 460.

in mean atomic density in the compressed regions near the center of the dislocation is less than the decrease in the extended regions. Thus the net result of having dislocations in the

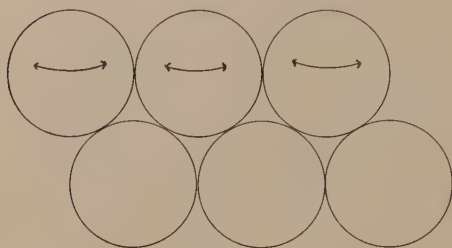


FIG. 2.

lattice is a decrease in density of the crystal. The relation between this decrease in density and the distortional energy associated with dislocations may, of course, be derived in the phenomenological manner followed by Professor Zener.

C. ZENER (author's reply).—The oral dis-

cussion has been ably answered by Professor Nielsen.

Dr. Lester and Professor Mathewson have suggested that the expansion of a distorted lattice may be thought of as resulting from the individual atoms seeking positions of minimum potential energy. Such an atomistic viewpoint leads to a very clear understanding of the expansion. Let us consider the relative displacement in shear of two adjacent rows of atoms in a close-packed plane, as in Fig. 2. If the atoms in lower row are kept fixed, a pure shearing stress will displace the upper atoms, not along a straight line but along the arc of a circle. The arcs have been drawn in Fig. 2 for the particular case of copper, the radius of curvature being computed from the information in ref. 8 and in Table 1. The curvature of these arcs is of the order of magnitude that one would expect from the naive picture of atoms sliding over one another.

Professor Seitz has given a beautiful picture of how cold-work may leave some regions in compression, others in extension.

Rate of Growth of Intermediate Alloy Layers in Structurally Analogous Systems

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(New York Meeting, February 1942)

THE formation of intermediate phase layers in cementation processes has been subjected to extensive qualitative investigation though to relatively little quantitative study; this work has recently been fully summarized by F. N. Rhines.¹ It is necessary here only to enumerate the general conclusions drawn concerning the kinetic laws governing the growth of intermediate layers and to state what is known concerning the structural changes accompanying the generation of phase layers.

1. When the intermediate phase is protective in type—i.e., when its density is less than that of the base metal, so that a continuous coating is formed and maintained—the isothermal growth of the phase follows a simple parabolic equation:

$$X^2 = kt \quad [1]$$

where X is the thickness of the alloy layer, k the reaction rate constant, and t the time. The applicability of this equation to diffusion processes is tested by plotting the square of the thickness versus time, or by plotting the thickness versus the square root of time; the resultant achievement of a straight line in such a plot has been considered sufficient proof of the validity of this equation. Exceptions have been found where liquid phases are involved in the

reaction, where the diffusion layer is cracked,² and where *thin* semimetallic oxide and sulphide coatings are formed on metals.³ In the first two cases the thickness increases linearly with time, and in the latter it is a logarithmic function of time.

2. The rate of thickening varies with temperature according to the Arrhenius equation:

$$k = Ae^{-Q/RT} \quad [2]$$

where k is the parabolic rate constant of Eq. 1, or some other rate-descriptive function, A is the action constant, e the base of natural logarithms, Q the heat of activation, R the gas constant, and T absolute temperature. This equation has been found to be generally valid except when transformations occur during reaction in either the base metal or in the reaction layer; in such instances Eq. 2 is still applicable with different values for the constants A and Q above and below the transformation temperature.

3. All phases that are stable at the temperature at which diffusion occurs will appear in the interdiffusion of two components. In some cases certain of the phases may be too thin to be observed and identified easily. Nonequilibrium phases have never been noted in *thick* reaction layers; i.e., layers of a thickness that may be discerned microscopically. The relative thickness of each phase in a diffusion layer is proportional to the concentration gradient and to the rate of diffusion in that phase.⁴ The reaction layers tend to have a

Manuscript received at the office of the Institute Dec. 1, 1941. Issued as T.P. 1463 in METALS TECHNOLOGY, 1942.

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¹ References are at the end of the paper.

grain structure that is columnar in the direction normal to the phase interface.

4. In the diffusion of a metal into a binary alloy, all single-phase and double-

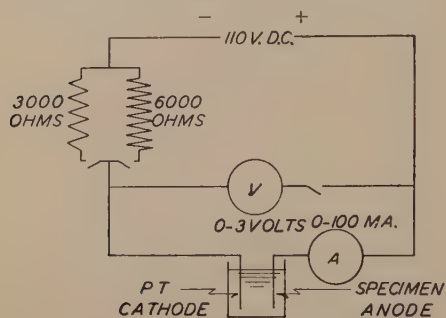


FIG. 1.—ELECTROLYTIC STRIPPING CIRCUIT.

phase regions that intersect the line connecting the composition of the binary alloy with the third element on an isothermal ternary section at the reaction temperature¹ will appear in the reaction layer.

The present study was undertaken to test the validity of these conclusions and also to procure quantitative data, now lacking, on the rates of interaction of various metal systems, particularly structurally analogous systems. Data on rates of formation of intermediate phases are available only for the systems Fe-Zn, Cu-Zn, Cu-Cd, Ag-Zn, and Ag-Cd,⁵⁻⁷ and, as will be shown later, the interpretation of the experimental results is doubtful. In the present work the rates of alloy formation in the systems Cu-Zn, Cu-Cd, Ni-Zn, Ni-Cd, Ag-Zn, Ag-Cd, Au-Zn, Au-Cd, Co-Zn, Fe-Zn, Monel-Zn, and Monel-Cd are determined.

The experimental approach to this problem resolved itself into two parts: (1) the identification of the phases present in the reaction layer, and (2) the determination of the rates of formation. The results will be discussed under these general subdivisions.

EXPERIMENTAL METHODS

Stripping Method.—The reaction times and temperatures used were such as to

yield reaction layers ordinarily too thin to be identified either chemically or by X-ray diffraction. For purposes of identification and, in one case, for the determination of

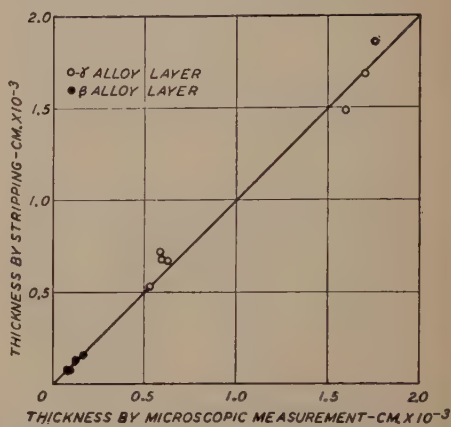


FIG. 2.—COMPARISON OF ALLOY THICKNESSES DETERMINED BY STRIPPING AND MICROSCOPICALLY.

phase thickness, resort was taken to the method of electrolytic stripping first devised by Glazunov⁸ for the analysis of galvanized coatings and later applied to the same coatings by Britton⁹ and Kenworthy.¹⁰

The electrolytic stripping method involves anodic attack by a constant impressed current, with the time required for the dissolution of each phase proportional to the thickness of that phase. The method is applicable where the coating phases are electrochemically less noble than the base metal in the solution used. The apparatus employed is shown schematically in Fig. 1. The voltmeter is a recording instrument and a typical voltage-time trace is shown in Fig. 4a, for a heated nickel-zinc couple. It will be noted that as each phase layer is revealed, the voltage changes discontinuously. The voltage drop across the cell of Fig. 1 consists in the sum of the voltage involved in the cathodic deposition, the resistance drop through the solution, and potential (or polarized potential) of the anode phase with respect

to the solution. The first two remain virtually constant, while the third varies according to the potential of the phase exposed at the anode.

The thickness of each phase may be calculated from the following equation, derived from Faraday's law:

$$l = \frac{It}{A} \cdot \frac{M}{Fd}$$

where l is the phase thickness, I the current, t the time, A the anode area, M the electrochemical equivalent of the metal or alloy phase, d the phase density, and F Faraday's constant. Since the density may be calculated from crystallographic data, phase thicknesses may readily be derived. In Fig. 2, the thicknesses of the phases formed in several nickel-zinc combinations determined by stripping are compared with the thicknesses measured microscopically; the correspondence between the two is good.

Electroplating and Heat-treating Procedure.—Specimens of Armco iron, grade A nickel, silver (analyzing 99.99 per cent Ag), chemically purified gold, commercial Monel, and copper (OFHC grade) were etched so as to show grain contrast, and each plated with zinc from a zinc chloride bath, or with cadmium from a cadmium cyanide bath. The base-metal thicknesses varied from 0.01 to 0.026 in. and the electroplates were approximately 0.008 in. thick; the electroplating baths were prepared from C.P. chemicals and were of standard composition. Approximately 0.005 in. of cobalt was plated from a standard cobalt sulphate bath on an iron sheet and the cobalt in turn was plated with zinc or cadmium. The rates of alloy formation in the combination Ni-Sn were determined on iron sheets plated with 0.0001 in. Ni from a sulphate bath and 0.0001 in. Sn from a sodium stannate bath.

The heating temperatures were below the melting points of zinc and cadmium. Heat-treating was carried out in oil baths

for the cadmium combinations and salt baths for the zinc combinations. Temperatures were controlled to $\pm 2^\circ\text{C}$. All specimens in which the electroplate or base metal were entirely consumed were excluded from rate studies; specimens in which the electroplates separated from the base metal were discarded.

IDENTIFICATION OF PHASES

*Nickel-zinc System**

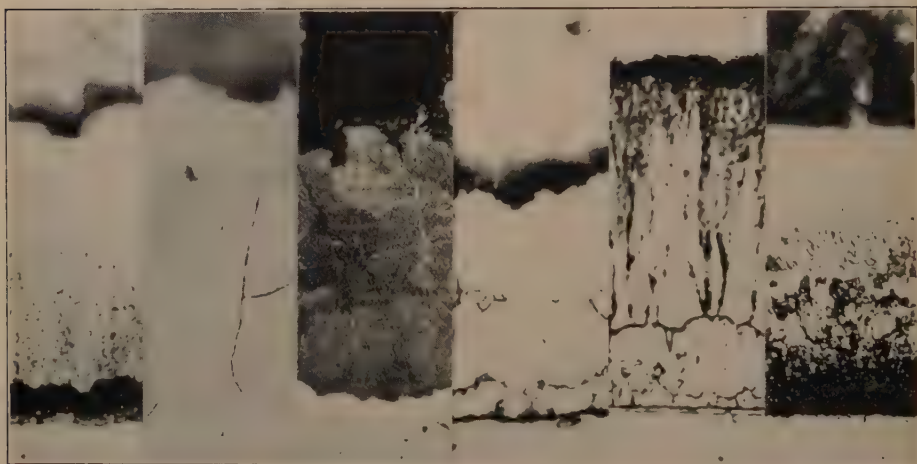
The nickel-zinc phase diagram¹¹ reveals four intermediate phases stable below the melting point of zinc; β_1 , γ_1 , γ , and δ . The β_1 phase is body-centered tetragonal with an atomic composition NiZn. The γ phase, $\text{Ni}_5\text{Zn}_{21}$, is structurally analogous to γ brass. The δ phase, $\text{Ni}_4\text{Zn}_{31}$, is analogous to δ brass. γ_1 is crystallographically a slightly distorted form of γ .

Fig. 3a shows the phase layers appearing in the interdiffusion of nickel and zinc. Fig. 4a gives a typical stripping curve of a nickel-zinc combination. Five arrests may be noted—at cell potentials of 0.3, 0.55, 1.4, 1.9, and 2.6 volts. A sixth arrest is often noted at 0.75 volts. These are the voltages accompanying a current density of 30 to 40 ma. per sq. cm. To allocate each arrest to the corresponding phase in the Ni-Zn system, a series of alloys of various compositions were prepared and their voltages measured in the cell shown in Fig. 1; the results are shown in Fig. 5. It may be observed that in two-phase regions the potential is constant at the potential of the more electronegative component, while in single-phase regions it increases with increasing nickel content.

* Where the phase diagram of the system in question is contained in the A.S.M. Metals Handbook (1939 Edition), the nomenclature of the phases adopted will conform to that diagram. Otherwise the nomenclature used by M. Hansen (Aufbau der Zweistofflegierungen) will be employed. Where, in either reference, structurally analogous phases are not designated by the same Greek letter, the phase nomenclature of the Cu-Zn system will be used.



- a.* Nickel-zinc heated at 367°C. for $\frac{1}{4}$ hr. $\times 2500$. Nital etch.
b. Nickel-cadmium heated at 289°C. for 3 hr. $\times 1000$. Iodine etch.
c. Copper-zinc heated at 367°C. for $\frac{1}{4}$ hr. $\times 2500$. $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$ etch.
d. Copper-cadmium heated at 289°C. for $6\frac{1}{2}$ hr. $\times 2500$. Iodine etch.
e. Silver-zinc heated at 394°C. for 1 min. $\times 2000$. $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$ etch.
f. Silver-cadmium heated at 258°C. for 6 hr. $\times 1500$. Iodine etch.



- g.* Cobalt-zinc heated at 394°C. for $\frac{1}{4}$ hr. $\times 2500$. Glycerin + HNO_3 + HF etch.
h. Gold-zinc heated at 367°C. for $\frac{1}{4}$ hr. $\times 1000$. $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$ etch.
i. Gold-cadmium heated at 258°C. for 13 hr. $\times 500$. Iodine etch.
j. Iron-zinc heated at 394°C. for $\frac{1}{4}$ hr. $\times 2500$. Glycerin + HNO_3 + HF etch.
k. Monel-zinc heated at 394°C. for $\frac{1}{4}$ hr. $\times 2500$. $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$ etch.
l. Monel-cadmium heated at 314°C. for 3 hr. $\times 1000$. Iodine etch.

The zinc or cadmium layer is at the top of all figures.

FIG. 3.—MICROSTRUCTURE OF PHASE LAYERS.

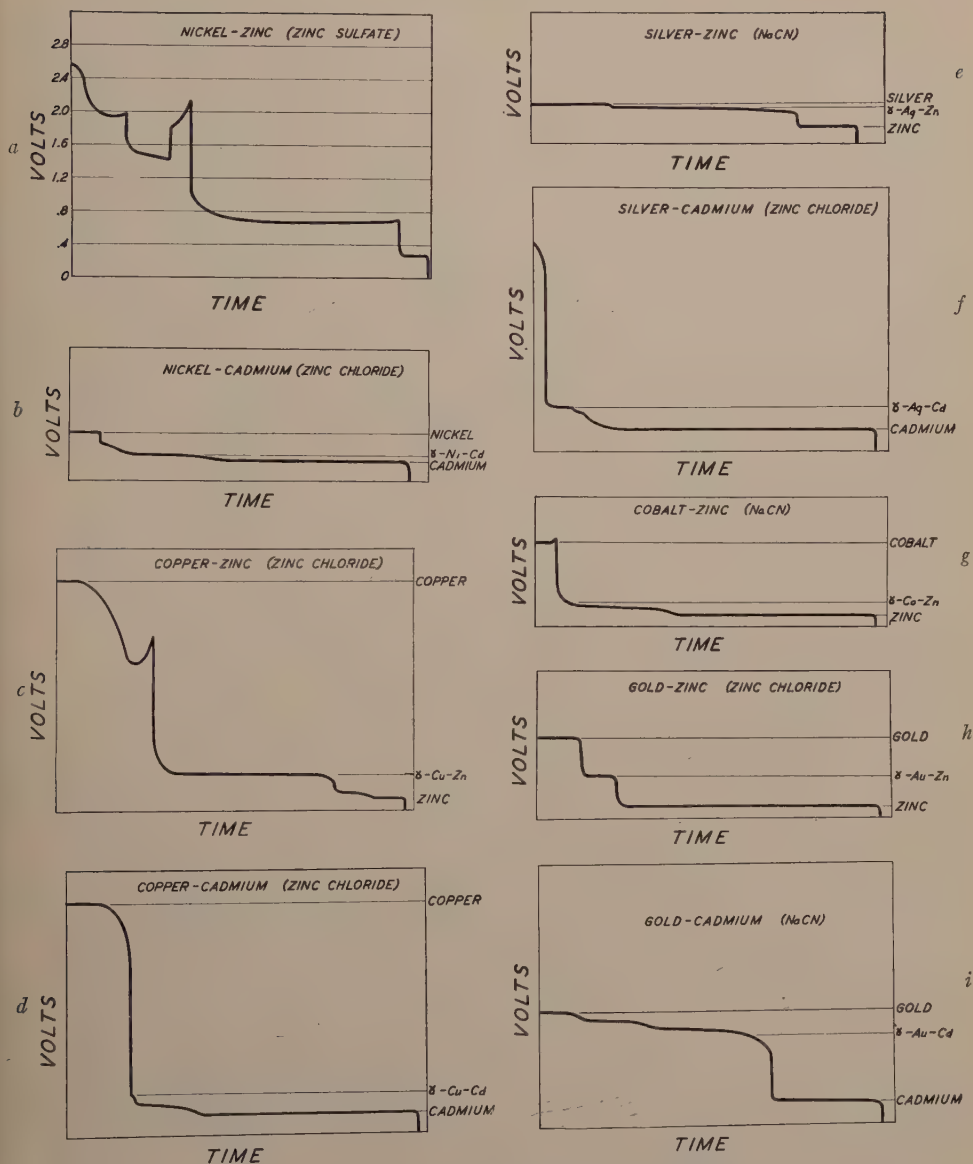


FIG. 4.—ELECTROLYTIC STRIPPING CURVES.

- a.* Nickel-zinc in zinc sulphate solution.
- b.* Nickel-cadmium in zinc chloride solution.
- c.* Copper-zinc in zinc chloride solution.
- d.* Copper-cadmium in zinc chloride solution.
- e.* Silver-zinc in sodium cyanide solution.
- f.* Silver-cadmium in zinc chloride solution.
- g.* Cobalt-zinc in sodium cyanide solution.
- h.* Gold-zinc in zinc chloride solution.
- i.* Gold-cadmium in sodium cyanide solution.

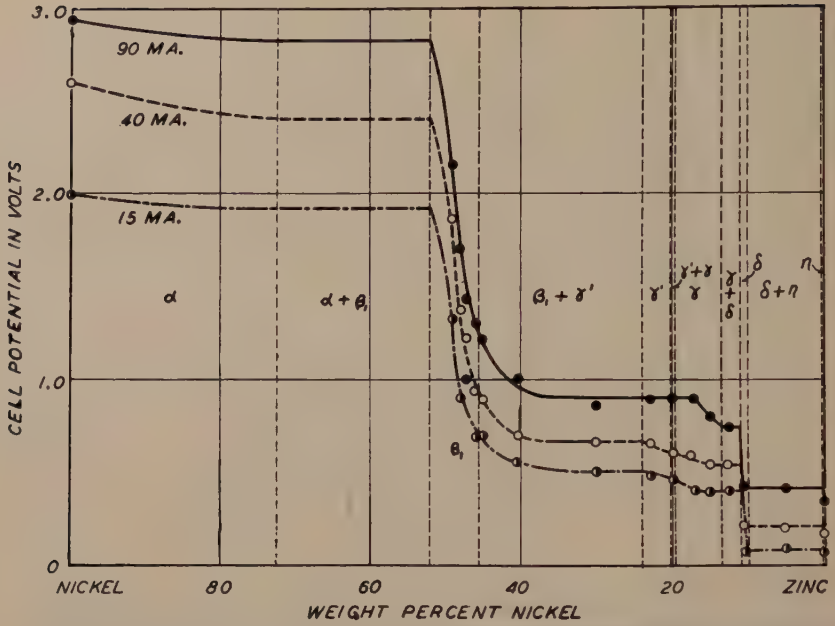


FIG. 5.—VARIATION OF ELECTROLYTIC STRIPPING CELL POTENTIAL WITH COMPOSITION FOR NICKEL ZINC ALLOYS.

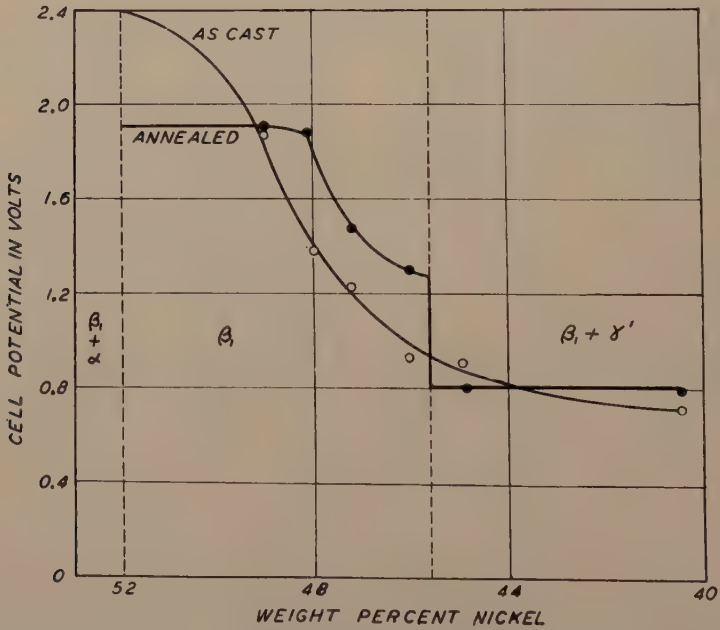


FIG. 6.—POTENTIALS OF NICKEL-ZINC ALLOYS AS CHILL CAST AND AS ANNEALED.

It may be concluded that the arrest at 0.3 volts corresponds to the solid solution terminal to zinc, those at 0.55 and 0.75 volts to the γ and γ_1 phases, respectively; those at 1.4 and 1.9 volts to compositions within the β_1 range, and the final arrest at 2.6 volts to the solid solution terminal to nickel. No arrest that might be attributed to the δ phase was noted; it appears that this phase either does not form or that it is too thin to be discovered in this way. Thus, in Fig. 3, the very thin layer next to nickel is the β_1 phase, and the thick succeeding layer consists of the γ_1 and γ phases.

It was noted above that two quite definite arrests often occur at 1.4 and 1.9 volts, voltages that are both within the apparently single-phase β_1 range. The as-cast alloys in the β_1 range (which were cooled rapidly by casting in a thick-walled iron mold) were annealed for 2 days at 675°C. and 5 days at 400°C., then cooled slowly to room temperature. The resultant cell potentials are shown in Fig. 6. On annealing, the potential curve within the β_1 range splits into two distinct parts—one at 1.3 to 1.5 volts and the other at 1.9 volts, corresponding to the potentials of the two β_1 arrests. Apparently the so-called β_1 phase is not electrochemically homogeneous. Fig. 6 may indicate either a sort of resistance limit in β_1 or a phase change. X-rays revealed no difference in crystal structure between the various β_1 alloys, although superlattice transformations, which would not be revealed by ordinary X-ray technique, might occur in these alloys. It should be noted here that Schramm¹² found an abrupt change in the lattice dimensions of the β_1 phase at approximately the same place as the change in potential shown in Fig. 6.

Nickel-cadmium System

The complete nickel-cadmium system has not been determined; the existence of a gamma phase, $\text{Cd}_{21}\text{Ni}_5$, structurally analogous to the γ phases of Cu-Zn and Ni-Zn,

has been established.¹³ In the interdiffusion of nickel and cadmium only one microscopically visible phase layer may be recognized, as shown in Fig. 3*b*. A stripping curve for the nickel-cadmium system is shown in Fig. 4*b*. Only one definite arrest may be observed; the potential of a γ Ni-Cd alloy coincided exactly with that of the arrest. Apparently, in the interaction of nickel and cadmium the γ phase alone is formed.

Copper-zinc System

In the copper-zinc system (p. 1367 of ref. 11) three intermediate phases appear at temperatures below the melting point of zinc—a body-centered cubic β_1 phase, CuZn, a cubic γ phase, Cu_5Zn_8 , structurally analogous to the γ phases of the Ni-Zn and Ni-Cd systems, and a close-packed hexagonal ϵ phase, CuZn_3 . A photomicrograph of the diffusion layer is shown in Fig. 3*c*; Fig. 4*c* gives a stripping curve. In the latter, three intermediate phases appear, the potential of the middle one corresponding to that of the γ phase; it is thus probable that the three intermediate phases forming are the β , γ , and ϵ phases. The last two may be observed in Fig. 3*c* (the β_1 phase was found to be present, but was much thinner than the other two phase layers).

Copper-cadmium System

In the Cu-Cd system (p. 1346 of ref. 11) four phases are stable below the melting point of cadmium. Of these only the γ phase, Cd_5Cu_5 (called δ in the diagram) is structurally analogous to phases in the Cu-Zn, Ni-Zn, and Ni-Cd systems. In Fig. 3*d* two phases may be noted in the diffusion layer, the higher-cadmium phase being the thicker. From the stripping curve of Fig. 4*d*, the inner layer is probably the γ phase and the outer the ϵ phase. The ϵ layer shows columnar grains characteristic of the formation of diffusion layers.

Silver-zinc System

At temperatures below the melting point of zinc, four intermediate phases appear (p. 1784 of ref. 11). The γ and ϵ phases are

The microscopic appearance of the AgZn phase at temperatures near the $\beta \rightleftharpoons \xi$ transformation was curious. The ξ phase formed at low temperatures is white,

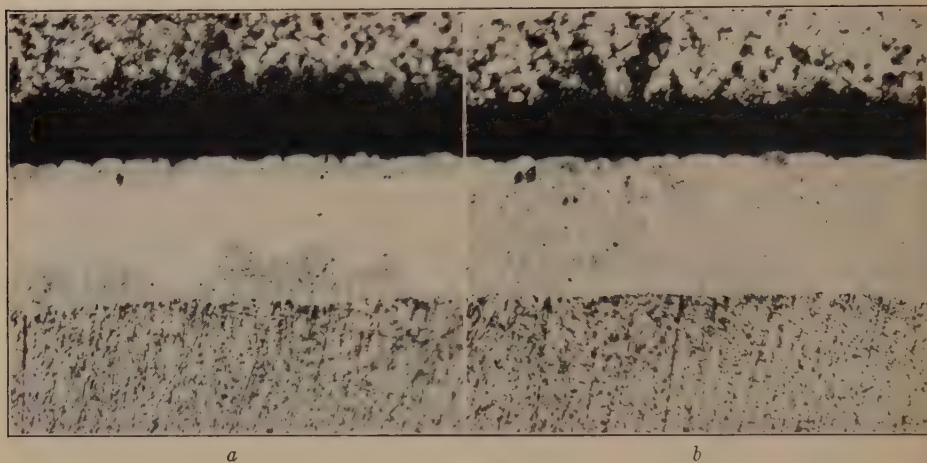


FIG. 7.—(a) SILVER-ZINC HEATED AT 280°C. FOR $\frac{1}{2}$ HOUR $\times 750$. $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$ ETCH; (b) SILVER-ZINC HEATED AT 314°C. FOR $\frac{1}{4}$ HOUR $\times 750$. $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$ ETCH.

structurally analogous to the γ and ϵ phases of the Cu-Zn system. The β phase (stable above 240° to 260°C.) is analogous to β CuZn, while the ξ phase (stable below 240° to 260°C.) is hexagonal and has no counterpart in Cu-Zn alloys. In the photomicrograph (Fig. 3e) three phases may be noted; however, the corresponding stripping curve (Fig. 4e) shows only one arrest. N. Puschin (p. 73 of ref. 13) found from electromotive force measurements that aside from a slight electromotive force jump at the α -phase boundary, the voltage of the Ag-Zn phases is independent of composition from 0 to 60 per cent Zn. Only within the ϵ phase does the voltage vary, and even then appreciably only at a composition of 71 per cent Zn. The deviation in the voltage of the arrest at the high-zinc end of the stripping curve indicates thus that the phase next to the zinc is the ϵ phase. It may be concluded, therefore, that the three-phase layers of Fig. 3e are, in order of decreasing silver content, the β (or ξ), the γ , and the ϵ phases.

whereas the β phase is pink in color. At temperatures of 200°, 228°, and 258°C. the inner phase layer is white. However, at a reaction temperature of 289°C. and a reaction time of $\frac{1}{2}$ hr. there appear at the Ag- ξ interface regions of pink β AgZn (Fig. 7a). At longer heating times the entire AgZn layer becomes pink. After $\frac{1}{4}$ hr. at 314°C. (Fig. 7b) most of the AgZn layer is pink, with a slight amount of ξ phase remaining at the γ AgZn interface. Again, longer heating times convert the layer entirely to β AgZn. Thus, it should be noted that at temperatures of 289° and 314°C., both above the highest temperature at which ξ AgZn can exist (260°C.), considerable amounts of this phase appear. The general conclusion in the introduction drawn from previous work on the formation of intermediate phase layers that non-equilibrium structures cannot form in thick diffusion layers is, accordingly, not generally valid. It is likely that ξ AgZn is more easily nucleated at the very beginning of reaction than the β form. Thus a phase

layer consisting of hexagonal AgZn forms first; the stable β form nucleates later at the Ag- ξ -AgZn interface and grows into the ξ phase until the latter is entirely consumed.

tered cubic structure. From this it may be concluded, first, that the data of Durrant placing the β' transformation at 230° to 240°C. is more accurate than previous

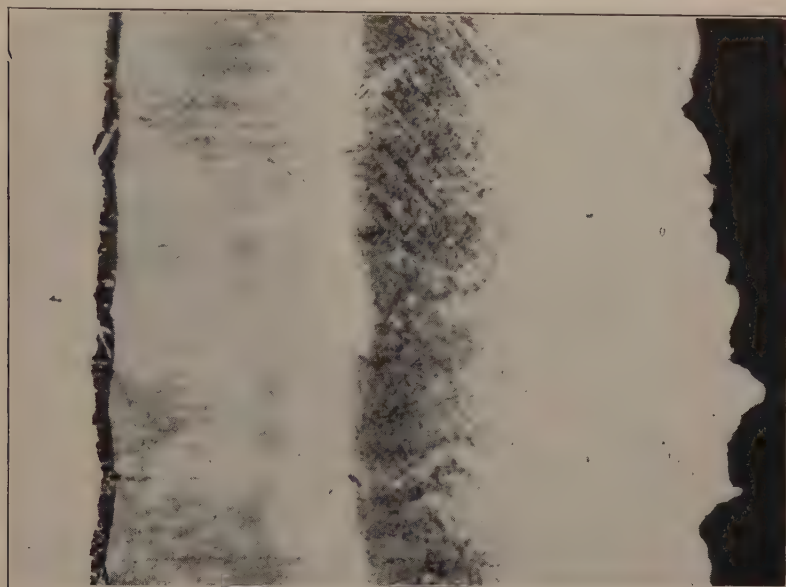


FIG. 8.—SILVER-CADMIUM HEATED AT 228°C. FOR 22 HOURS. $\times 1500$. IODINE ETCH.

Silver-cadmium System

The Ag-Cd system (p. 20 of ref. 13) shows four phases stable at temperatures below the melting point of cadmium—an ordered body-centered cubic β' -phase stable below 186° to 211°C. (or 230° to 240°C.), a hexagonal β_1 stable above this temperature, and γ and ϵ phases structurally analogous to those of the Cu-Zn system. Fig. 3f shows two phase layers. From the stripping curve of 4f it may be concluded that the outer layer is ϵ and the inner γ . Fig. 3f was taken at a reaction temperature of 258°C. , and it may be observed that no β layer is present; at this temperature the β_1 phase is hexagonal in structure. In Fig. 8, showing a specimen reacted at 228°C. , a very definite β layer is present; at this temperature according to the data of Durrant (p. 20 of ref. 12) the β' phase occurs with an ordered body-cen-

tered cubic structure. From this it may be concluded, first, that the data of Durrant placing the β' transformation at 230° to 240°C. is more accurate than previous data, which gave this transformation as occurring at 186° to 211°C. ; second, that either the diffusion rate in the hexagonal β_1 phase is exceedingly slow (which would seem an unjustified assumption) or that no β_1 phase exists in the Ag-Cd system and that a temperature gap exists between the ordered β' phase disappearing at 230° to 240°C. and the disordered β phase reappearing at 440° to 470°C.

Cobalt-zinc System

In the Co-Zn system, according to Schramm,⁸ four phases are stable at low temperatures; these are (in order of decreasing zinc content) ξ , structurally analogous with ξ -Fe-Zn; δ_1 analogous to δ Ni-Zn and δ Fe-Zn, γ , analogous to γ brass; and β_1 analogous to β_1 Ni-Zn. Fig. 3g shows three separate layers, while stripping curve Fig. 4g shows only one layer; it is possible that the other

layers were not revealed because of their slight thickness. It will be noted that γ Co-Zn has a voltage appreciably higher than that of the thick phase layer. Thus the

and the two thin layers probably are the β and α_1 (or α_2) phases (the latter next to gold). An unexpected phenomenon was noted in the heated Au-Zn plates; at

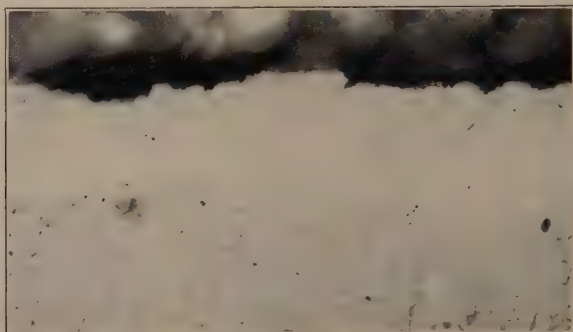


FIG. 9.—GOLD-ZINC HEATED AT 367°C. FOR $\frac{1}{4}$ HOUR. $\times 1000$. $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$ ETCH.

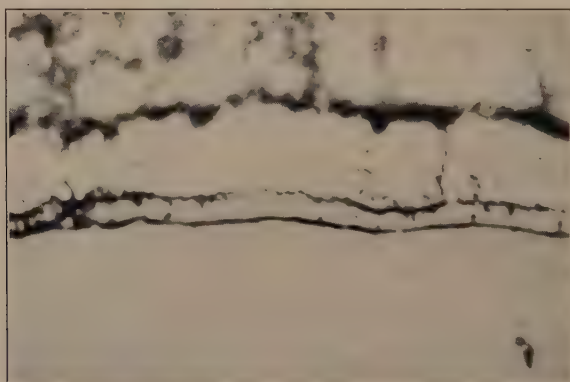


FIG. 10.—IRON-ZINC HEATED AT 314°C. FOR 3 HOURS. $\times 2500$. GLYCERIN + $\text{HF} + \text{HNO}_3$ ETCH.

outer layer is either ξ or δ_1 , the black middle layer probably γ , and the inner layer β_1 .

Gold-zinc System

The Au-Zn system (p. 268 of ref. 13) shows three intermediate phases, ϵ , γ , and β , which are structurally analogous to the corresponding Cu-Zn phases; the system is complicated by a number of superlattices in the α and γ ranges. Fig. 3*h* shows the occurrence of a very thick external layer, together with two thin layers next to the gold. The stripping curve Fig. 4*h* indicates that the thick layer is γ ,

certain places no γ alloy was present, while the α_1 and β alloys at such points were much thicker than usual. This may be seen by comparison of Figs. 9 and 3*h*, taken at different places on the same specimen. It is possible that the formation of γ at such places was prevented by some obstacle, such as an oxide layer, which prevented the diffusion of gold into zinc to form the γ layer, while zinc was free to diffuse into gold, forming the α_1 and β alloys. A similar phenomenon was noted in Cu-Zn alloys, the β phase tending to thicken at places at the expense of the γ and ϵ phases.

Gold-cadmium System

At low temperatures three intermediate phases are stable in the Au-Cd system (p. 210 of ref. 13). Again these are the ϵ , γ , and

δ , and γ phases, which are structurally analogous to the corresponding Co-Zn phases. In Fig. 3j three phase layers may be noted. It is thus probable that the inner

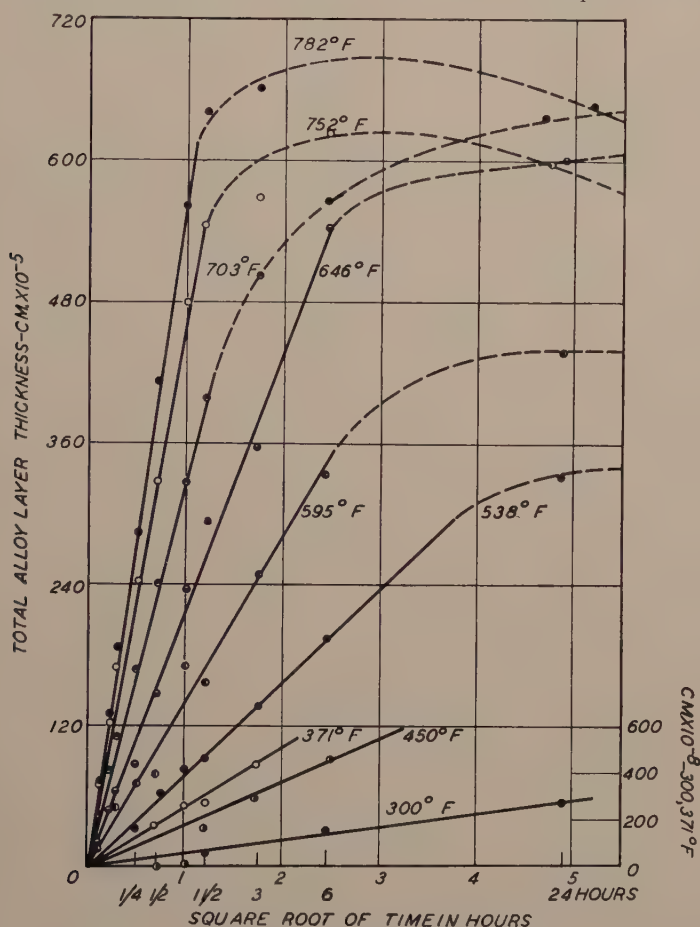


FIG. 11.—TOTAL ALLOY THICKNESSES IN NICKEL-ZINC COUPLES PLOTTED AS A FUNCTION OF SQUARE ROOT OF TIME.

β phases, which are structurally analogous to the ϵ , γ , and β phases in the Cu-Zn system. Comparison of Figs. 3i and 4i shows a thick layer of γ formed next to the zinc, with a β layer next to the gold.

one is γ , the middle δ , and the outer ξ . The δ phase forms only at temperatures above 337°C. Below this temperature, as shown in Fig. 10, only the γ and ξ phases appear.

Iron-zinc System

Three intermediate phases form in the Fe-Zn system (p. 1745 of ref. 11). These are, with increasing iron content, the ξ ,

Monel-zinc

In Fig. 3k are shown the diffusion layers resulting from the diffusion of zinc into Monel. Four layers may be distinguished, a

thick outer layer showing columnar grains and three succeeding layers of diminishing thickness. If the Cu-Ni-Zn system¹⁸ is analyzed by the method of Rhines¹ (p.

outer part of the external layer (next to the zinc) possibly consists of a $\delta + \text{Zn}$ mixture; progressing inward, the amount of zinc as judged by the darkening becomes

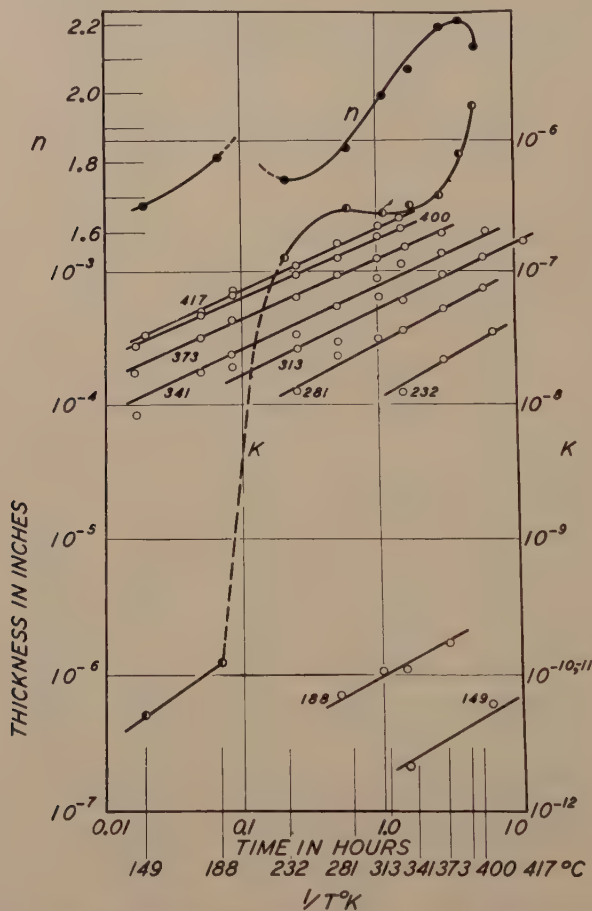


FIG. 12.—LOG OF ALLOY THICKNESS FORMED IN NICKEL-ZINC COUPLES PLOTTED VS. LOG OF TIME (OPEN CIRCLES). VARIATION OF REACTION INDEX n (BLACK CIRCLES) PLOTTED AS FUNCTION OF $\frac{1}{T^{\circ}\text{K}}$ AND REACTION CONSTANT K (HALF-FILLED CIRCLES).

1374 of ref. 7) for the sequence of layers appearing in the diffusion of zinc into a 67 per cent Ni alloy, the following sequence of phases should occur, starting with the zinc end: first, a two-phase $\delta\text{-Ni-Zn} + \text{Zn}$ layer, then a δ layer, a $\gamma + \delta$ layer, γ , β , and finally an $\alpha + \beta$ layer. Such a sequence may be inferred from Fig. 3*k*. The dark

less, until an apparently single-phase δ layer is reached. The succeeding layer may be observed to contain small particles and may well be the $\gamma + \delta$ layer; the final layers are thus γ and β . In this case the conclusion reached by Rhines¹ as to the structure of ternary diffusion layers would seem justified.

Monel-cadmium System

In the diffusion of cadmium into Monel the diffusion layer shown in Fig. 31 is obtained. It may be observed that a white

stable at low temperatures; these are Ni_3Sn_4 , Ni_3Sn_2 , and Ni_3Sn . Each of these may be identified in a nickel-tin diffusion layer. The Ni_3Sn_4 layer was found to form

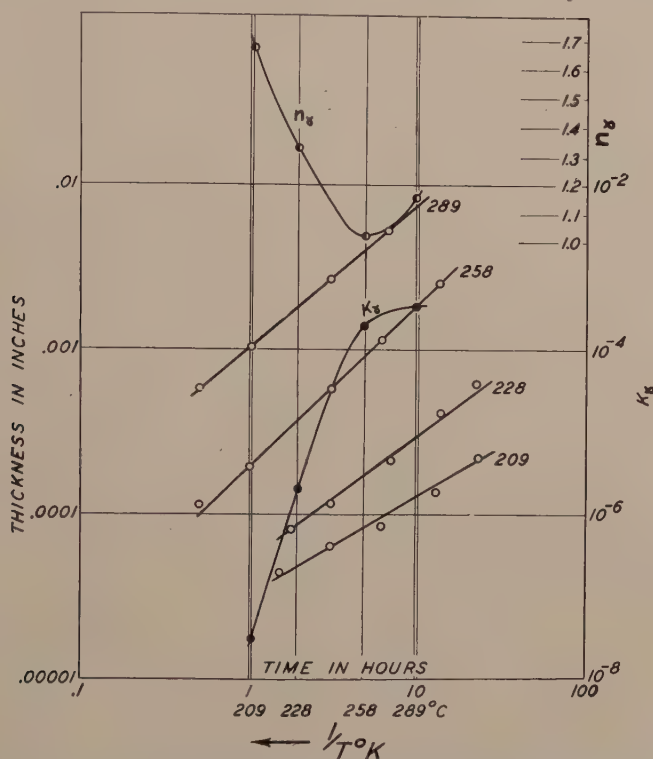


FIG. 13.—LOG OF ALLOY THICKNESS FORMED IN NICKEL-CADMIUM COUPLES PLOTTED VS. LOG OF TIME (OPEN CIRCLES). VARIATION OF REACTION INDEX n (HALF-FILLED CIRCLES) AND REACTION CONSTANT K (CLOSED CIRCLES) PLOTTED AS FUNCTION OF $1/T^\circ\text{K}$.

single-phase external layer is followed by a two-phase layer consisting of white equiaxed grains in a matrix of the external phase. In the succeeding two-phase layer a dark-etching phase surrounds the white, equiaxed grains, the latter gradually disappearing, leaving an apparently single-phase black layer adjacent to the Monel. Since no information is available on the ternary Cu-Ni-Cd diagram, identification of the phases appearing in this layer is not possible.

Other Systems

In the nickel-tin system (p. 1638 of ref. 11) three intermediate phases are

in discontinuous patches, while Ni_3Sn was formed only after prolonged heating.

No Fe-Cd or Co-Cd diffusion layer was observed in the heating times and temperatures used.

RATES OF FORMATION OF INTERMEDIATE PHASES

Nickel-zinc System

The total thickness of the intermediate phase layers formed on diffusion are plotted in Fig. 11 as a function of the square root of time. If Eq. 1 is obeyed, a straight line should be obtained. The data fit quite well on straight lines except for deviations at

large thicknesses formed on long annealing; on such a treatment the zinc coating is consumed and such a deviation is to be expected.

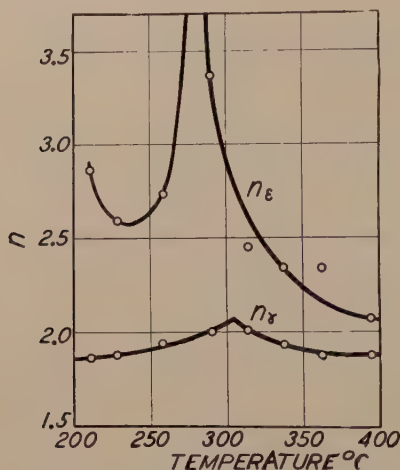


FIG. 14.—VARIATION OF REACTION INDICES FOR ϵ AND γ COPPER-ZINC WITH TEMPERATURE.

Let us assume, however, that instead of the simple parabolic equation,

$$X^2 = kt \quad [1]$$

a general parabolic equation of the form

$$X^n = Kt \quad [3]$$

may be taken to represent the data, where X is again thickness, n may be called the reaction index, and K the reaction constant. A plot of the logarithm of thickness versus the logarithm of time should, if Eq. 3 is applicable, yield a straight line

whose slope is $\frac{1}{n}$, and whose intercept at one hour (the logarithm of thickness attained in one hour) multiplied by n gives the logarithm of K in units of thickness n per hour.

In Fig. 12 the data employed in Fig. 11 are plotted as the logarithm of thickness in inches vs. logarithm of time (open circles). All the points lie on straight lines,

indicating the validity of the general parabolic equation. If the slopes of these lines are determined, it is found that the reaction index n (closed circles, Fig. 12) no longer has a constant value of 2 but varies with temperature from 1.6 to 2.2 in the manner shown. It thus becomes apparent that the simple parabolic equation (Eq. 1) is not generally valid for the formation of reaction products on metals, and that methods of plotting data designed solely to test the applicability of the *simple* parabolic equation (Eq. 1) are misleading and insensitive.

If the simple parabolic equation (1) were obeyed, then the Arrhenius equation (2) follows, and $\log K$ vs. $1/T$ would provide a straight line. If, however, Eq. 3 were obeyed, and if the exponent n were a function of temperature, the Arrhenius equation would no longer necessarily follow. The plot in Fig. 12 shows that the latter condition prevails. Since, then, n varies with temperature in a complicated way, and since also a variation in n will exert a powerful influence on K , it is not surprising that $\log K$ should vary with $1/T$ in a complicated fashion.

Nickel-cadmium System

In Fig. 13 the data on rate of interaction of nickel with cadmium are analyzed in the same manner. It will be recollected that cadmium forms only a γ phase on reaction with nickel at low temperatures; thus the curves of Fig. 13 refer to the rate of growth of the γ -Ni-Cd phase. The reaction index n deviates even more greatly than in nickel-zinc from the value 2 required by classical diffusion laws: n lies always below the "kinetic equilibrium" value of 2. The reaction index apparently passes through a minimum with increasing temperature while the reaction constant K shows a maximum. In general, the curve of reaction constant vs. temperature will have the shape of the inverse of the reaction index-temperature curve.

Copper-zinc System

In Fig. 14 the course of the reaction-index-temperature curves for the ϵ and

value of 2, and that a discontinuity apparently exists at a temperature of about 280°C . n_γ , however, does not deviate

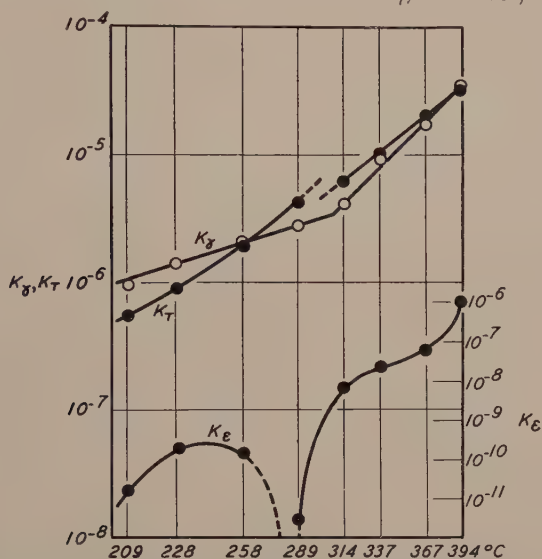


FIG. 15.—LOG OF REACTION CONSTANTS FOR TOTAL DIFFUSION LAYER¹ (BLACK CIRCLES), γ BRASS (OPEN CIRCLES) AND ϵ BRASS (CLOSED CIRCLES) PLOTTED VS. $1/T^\circ\text{K}$.

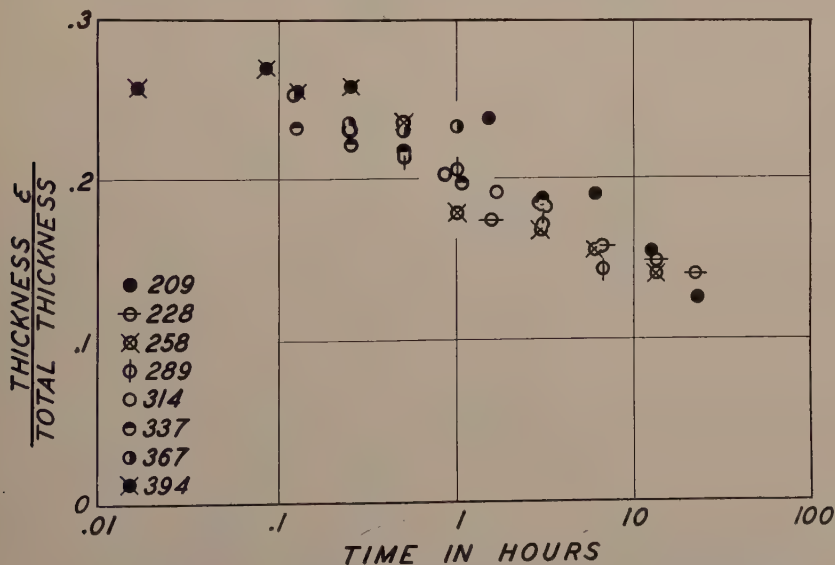


FIG. 16.—VARIATION OF RELATIVE ϵ -BRASS LAYER THICKNESS WITH REACTION TIME.

γ phases of the Cu-Zn diffusion layer are depicted. It will be observed that n_ϵ differs greatly from the "kinetic equilibrium"

greatly from a reaction index value of 2; it shows a slight but definite maximum at approximately 310°C . The reaction con-

stants are plotted in Fig. 15. The reaction constant for the total diffusion layer shows a break at 289° to 314°C. The curve of $\log K_\gamma$ vs. the reciprocal of absolute

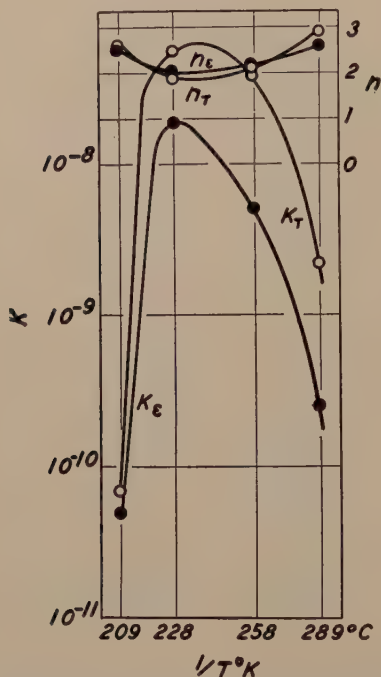


FIG. 17.—CHANGE IN REACTION INDICES FOR ϵ LAYER (CLOSED CIRCLES) AND TOTAL COPPER-CADMIIUM DIFFUSION LAYER (OPEN CIRCLES) AND IN THE LOG OF THE CORRESPONDING REACTION CONSTANTS K_ϵ AND K_T WITH $\frac{1}{T^\circ K}$.

temperature resolves itself into two straight lines intersecting at 310°C. This indicates strongly that a change in phase occurs in the gamma phase at this temperature. Indeed, reference to the literature confirms this evidence. Matsuda (p. 666 of ref. 13) and Imai (p. 666 of ref. 13) found weak indication of a change in the γ phase at 250°–280°C. Johansson and Westgren (p. 266 of ref. 13) found also a change in the crystal structure of γ with composition. Thus low-temperature reaction-rate studies, and the analysis of data in the manner shown here, would seem a powerful tool

for the investigation of phase changes at low temperatures.

The variation of K_ϵ with temperature is shown in Fig. 15. This type of curve is greatly different from that of the γ phase. With increasing temperature K_ϵ first increases to a maximum and then decreases. An apparent discontinuity occurs at approximately 280°C. after which K_ϵ again increases. This type of temperature variation will be shown to be quite common. Indeed, for the case of nickel-zinc, the K_T variation in the temperature range 232° to 417°C. is a less pronounced version of the $K_\epsilon - \frac{1}{T}$ curve, while for nickel-cadmium the variation of K with temperature is similar to the first part of the $K_\epsilon - \frac{1}{T}$ curve. Hereafter the $K_{\gamma\text{Cu-Zn}} - \frac{1}{T}$ curve will be designated as the γ -type curve, and the other the ϵ -type.

It is a consequence of classical diffusion laws when applied to the formation of intermediate phases that the relative thickness of each phase should remain constant with reaction time at any given temperature. In Fig. 16 is plotted the ratio of ϵ to total diffusion-layer thickness; it will be noted that at all reaction temperatures the change in ratio depends only on time and not on temperature. Such a result further invalidates the application of classical diffusion laws to the rate of low-temperature diffusion-layer formation.

Copper-cadmium System

In the copper-cadmium diffusion layer the predominant phase is ϵ , with a slight amount of γ present adjacent to copper. The variation of n and K with temperature for the entire reaction layer and also for the ϵ phase alone is plotted in Fig. 17. The $\log K_\epsilon - \frac{1}{T}$ curve greatly resembles the first part of an ϵ -type curve. A thermal arrest has been noted in alloys of ϵ composition (p. 415 of ref. 13); this arrest was

observed at about $314^{\circ}\text{C}.$, which, by extrapolation, seems to be the temperature of the discontinuity in the $\log K - \frac{1}{T}$ plot for the ϵ phase.

at high temperatures. It would seem that ϵ Cu-Zn is more easily nucleated than γ Cu-Zn at all reaction temperatures, and thus tends to form in a ratio greater than its "kinetic equilibrium" ratio. At low

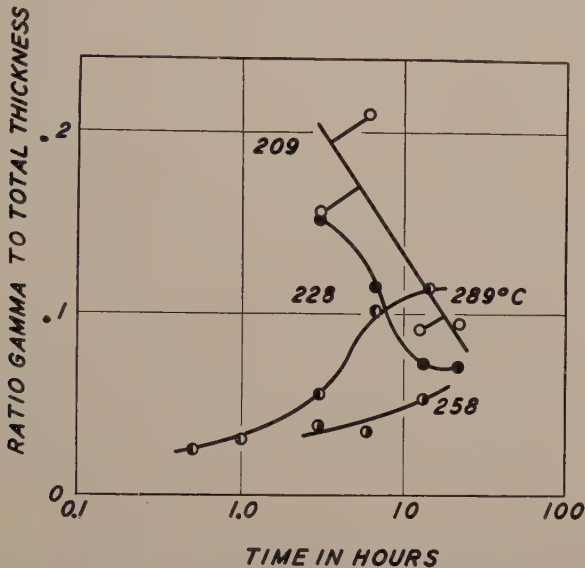


FIG. 18.—VARIATION OF RELATIVE γ COPPER-CADMIUM LAYER THICKNESS WITH TIME AT VARIOUS TEMPERATURES.

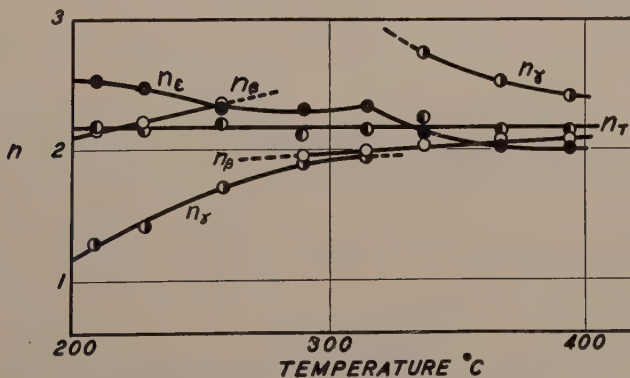


FIG. 19.—VARIATION WITH DIFFUSION TEMPERATURE OF REACTION INDICES FOR TOTAL SILVER-ZINC DIFFUSION LAYER, ϵ , γ , AND β LAYERS.

In Fig. 18 is shown the variation of the relative thickness of γ with time and temperature. In contrast to the results on the ϵ phase of copper-zinc, the relative amount of γ decreases with time at low temperatures, while it increases with time

temperatures γ Cu-Cd is more easily nucleated than ϵ Cu-Cd; at higher temperatures the reverse holds true. Thus the general conclusion that the relative thickness of any phase layer remains unchanged with time is invalidated.

Silver-zinc System

The reaction indices for the various phases in the Ag-Zn diffusion layer are shown in Fig. 19, while the corresponding

whereas the present type shows a discontinuous jump in the value of the reaction constant at a certain temperature; the slopes of the $\log K - 1/T$ curves above

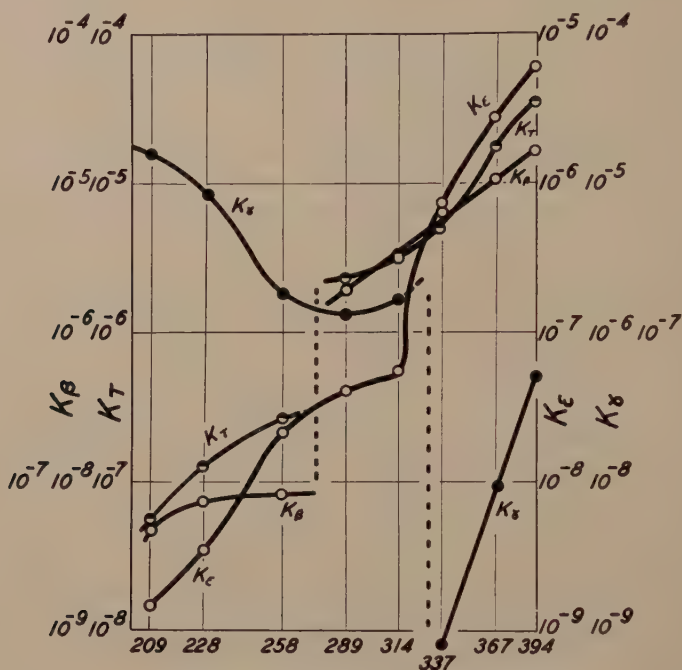


FIG. 20.—VARIATION OF LOG OF REACTION CONSTANTS WITH $\frac{1}{T^{\circ}K}$ FOR TOTAL SILVER-ZINC DIFFUSION LAYER, β , γ , AND ϵ LAYERS.

reaction constants are plotted in Fig. 20 as $\log K$ vs. $1/T$. The reaction index for the total reaction layer is constant; the reaction constant, however, shows a discontinuity at approximately 270°C . Both the reaction index and the reaction constant for the β phase show a discontinuity at about 270°C . The reaction constant for the β phase varies only slightly with temperature below 270°C .; above this temperature it obeys the Arrhenius equation (2). This type of curve (which may be associated with $\xi \rightleftharpoons \beta$ transformation) is similar to the γ -type curve. The essential difference between these two types of curve lies in the observation that a change in slope only may be observed in the γ -type

and below the discontinuity temperature again differ. This type of curve will be known as a β -type curve and is to be associated with changes of phase accompanied by an appreciable composition or structural change, while the γ -type curve shows a change in phase without appreciable change in composition or structure. Both n_s and K_s show a variation characteristic of γ -type curves while K_γ greatly resembles the ϵ -type.

Silver-cadmium System

Figs. 21 and 22 show, respectively, the variation of n and K for the various Ag-Cd phases. Both n_T and K_T (reaction constants for the total layer) show γ -type curves

with the inflection point at 258°C. This is probably to be related to the transformation of β' to β_1 with increasing temperature. K_ϵ shows an ϵ -type curve. However, the change of K_γ with temperature is different from any variation observed heretofore. The shape of this curve is roughly the inverse of the ϵ -type curve, and it will be designated as a $1/\epsilon$ -type curve. A superlattice transformation has been observed in the γ phase (p. 20 of ref. 12); this is, however, reported at an appreciably higher temperature than that of the discontinuity in the $\log K_\gamma - \frac{1}{T}$ curve.

Cobalt-zinc System

The diffusion layer in this system consists almost entirely of either the ξ or δ_1 Co-Zn phase; Fig. 23, showing the variation with temperature of the total alloy thickness, the reaction indices, and the reaction constants may thus be considered also as representative of the ξ phase (or δ_1). The variation here is of the $1/\epsilon$ -type. Schramm¹² found a transformation in the δ_1 phase by X-ray diffraction—this may well cause the variation of K and n observed in Fig. 23.

Iron-zinc System

In Fig. 24 the logarithm of the diffusion-layer thickness in the Fe-Zn system is plotted as a function of the logarithm of time. The very slight slope of the curves at the lower temperatures is particularly striking. This gives rise to the very large values of the reaction indices at low temperature shown in Fig. 25; n rapidly falls to smaller values with increasing temperature. n_γ and K_γ for the Fe-Zn diffusion layer indicate an ϵ -type curve.

Monel-zinc and Monel-cadmium

As shown in Fig. 26, the reaction constant for Monel-zinc varies with temperature according to an ϵ -type curve, while for

Monel-cadmium the Arrhenius equation (Eq. 2), seems to apply.

Summary of Reaction Rates

The preceding experiments have served to cast doubt on the general validity of the

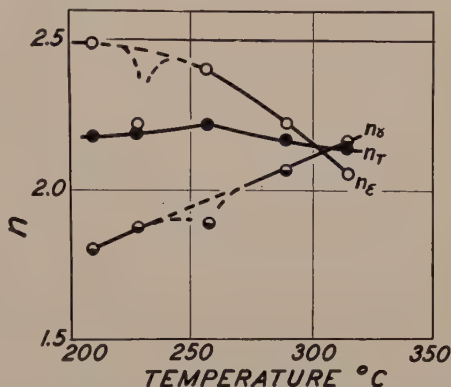


FIG. 21.—VARIATION WITH DIFFUSION TEMPERATURE OF REACTION INDICES FOR TOTAL SILVER-CADMIUM DIFFUSION LAYER, γ AND ϵ LAYERS.

simple parabolic equation (Eq. 1) and have instead established the reality of a general parabolic equation (Eq. 3). The variation of the reaction-rate constant K of the general parabolic equation is of five general types:

1. The ϵ -type, in which K with increasing temperature increases to a maximum, then decreases, and after a more or less pronounced discontinuity increases again.
2. The $\frac{1}{\epsilon}$ -type, in which K with increasing temperature either increases or decreases slightly and then jumps discontinuously to a high value from which it decreases.
3. The γ -type, in which K with increasing temperature shows a change in slope at a definite temperature.
4. The β -type, in which K increases with increasing temperature, but shows a discontinuity at a definite temperature.
5. The Arrhenius type, Eq. 2.

The various systems together with their types of temperature variations of K are listed in Table 1.

STRUCTURE SENSITIVITY IN FORMATION OF REACTION LAYERS AT LOW TEMPERATURES

High-temperature diffusion rates, as a general rule, are comparatively structurally

insensitive.¹⁴ At low temperatures, however, variations in grain size, distortion, or degree of imperfection (those features comprising structure in the term structure-

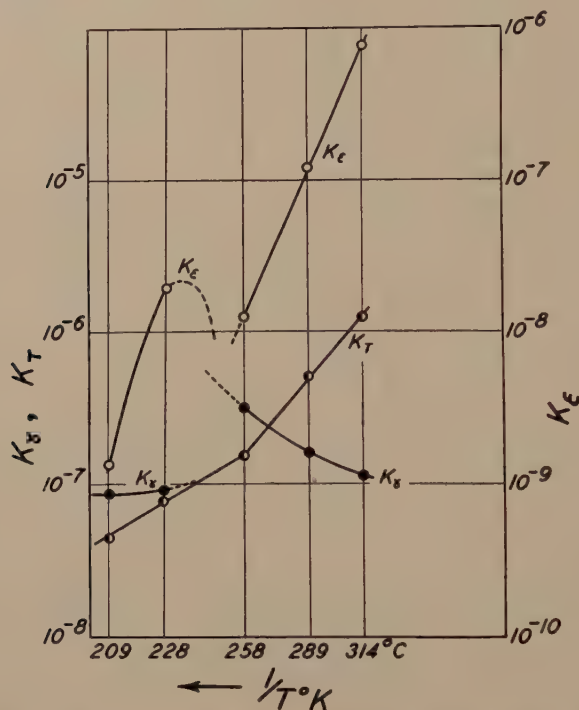


FIG. 22.—VARIATION WITH $\frac{1}{T^{\circ}K}$ OF THE LOG OF REACTION CONSTANTS FOR THE TOTAL SILVER-CADMIUM DIFFUSION LAYERS, γ , AND ϵ LAYERS.

TABLE I.—Temperature Variations of K

System	Phase	Type of Temperature Variation in K
Ni-Sn.....	Total layer (γ predominant)	ϵ
Ni-Cd.....	γ	ϵ
Cu-Zn.....	γ	γ
	ϵ	ϵ
Cu-Cd.....	ϵ	ϵ
Ag-Zn.....	γ	ϵ
	β	β
	ϵ	γ
Ag-Cd.....	ϵ	ϵ
	γ	ϵ/ϵ
Co-Zn.....	Total layer	γ
	Total layer (δ_1 or ϵ predominant)	ϵ/ϵ
Fe-Zn.....	Total layer	ϵ
Monel-Zn.....	Total layer	ϵ
Monel-Cd.....	Total layer	Arrhenius

sensitive) in either of the two metals may affect the rate of formation of diffusion layers. Fig. 27 shows a photomicrograph of a nickel block into which had been introduced an artificial crack; this sample was then zinc-plated and finally heated at 379°C. for 7 hr. The β_1 and γ alloy phases penetrate deeply not only along grain boundaries but also into the crack. This experiment shows the reaction to be structure-sensitive with respect to both grain size and gross imperfections.

Fig. 28 shows the effect of thickness of nickel and zinc on the rate of formation of the β_1 phase in the Ni-Zn system; the

rate of formation increases greatly as the nickel or zinc thickness is reduced. The increase is negligible beyond thicknesses of 0.001 in. for the times and temperatures

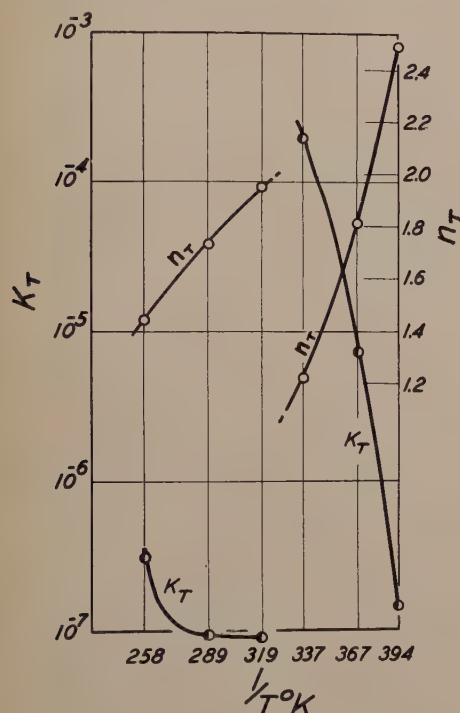


FIG. 23.—VARIATION WITH $\frac{1}{T^{\circ}K}$ OF THE REACTION INDEX FOR THE TOTAL COBALT-ZINC LAYER (n_T) AND OF THE LOG OF THE REACTION CONSTANT (K_T).

of reaction used. Such an effect is caused probably by solute saturation of the limiting phases rather than by any structure sensitivity. The latter effect may well play a part, however. It is characteristic of electroplates that their grain size tends to increase with thickness; thus the increase in the rate of reaction-layer formation with thin limiting phases may result in part from the faster diffusion along grain boundaries.

DISCUSSION OF RESULTS

At the outset of this work it was expected that the relative thicknesses of the

several phase layers formed by diffusion in the structurally analogous systems would be similar, though exhibiting differences in the rate of formation owing to differences

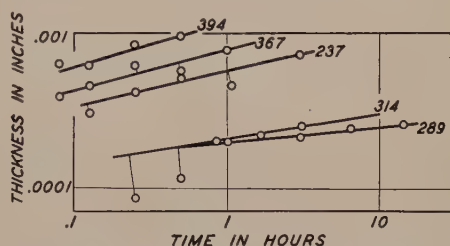


FIG. 24.—LOG OF TOTAL IRON-ZINC DIFFUSION LAYER THICKNESS PLOTTED VS. LOG OF TIME.

in the diffusion coefficients in the several systems. The first expectation was by no means realized, as the following examples show. In the Cu-Zn system the ϵ layer is approximately one third as thick as the γ layer, while the β_1 layer is only a very small fraction of the γ layer; in the system Ag-Zn, in which the structural analogies to the Cu-Zn system are most marked, the ϵ layer is two or more times as thick as the γ layer, and the β layer some five or six times as thick as the γ ; in the Ag-Cd system the ϵ and γ layers are of almost equal thickness, whereas the β layer is either absent or extremely thin; in the Au-Zn and Au-Cd systems no ϵ phase could be found, while the β phase of the latter system was very much thicker than that of the former. Similar differences may be noted in the iron, cobalt, and nickel systems. It must thus be concluded that in these intermediate phases the identity of lattice type and in many cases a near identity of concentration range in the respective phases are not sufficient to give similar ratios in the rate of formation of the separate phases; apparently the thickness ratios depend upon diffusion coefficients, which vary with the specific metals involved, or upon differing rates of transfer across phase interfaces, which likewise may vary from system to system. The latter possibility is unlikely, as will be shown below.

The *simple* parabolic equation (Eq. 1) is directly derived from Fick's law, the classic diffusion equation. A general parabolic equation (Eq. 3), which seems to be fol-

concurrently or intermittently—a highly unlikely circumstance—the rate index n might vary between 1 and 2; but this would provide no explanation for values of

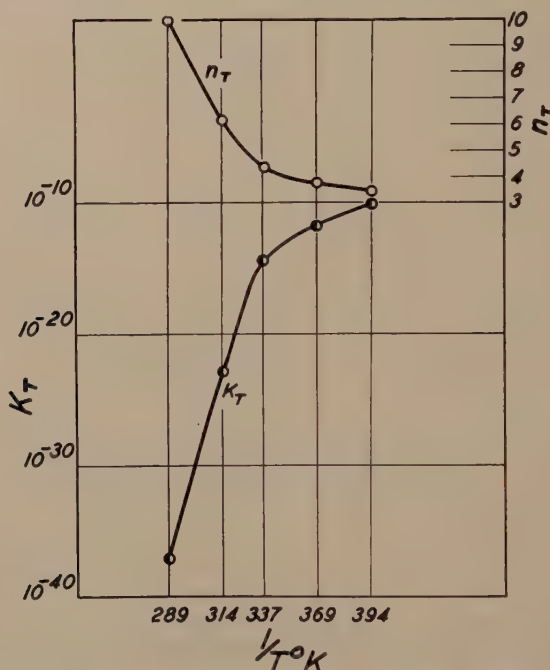


FIG. 25.—VARIATION OF n_T (REACTION INDEX FOR TOTAL IRON-ZINC SYSTEM) AND $\log K_T$ (REACTION CONSTANT) WITH $\frac{1}{T^\circ K}$

lowed by these reaction layers, cannot be deduced from Fick's law. In a case of this sort, where simple diffusion equations are inadequate to express the rate of transfer, the inclination is strong to ascribe the result to a rate of transfer across a phase interface slow enough in comparison to the diffusion coefficients to determine the over-all rate. However, in the case of a control of the rate of growth by an interface reaction, the rate must be independent of the thickness of the reaction product and must result in a linear time law of growth; i.e., in a parabolic equation with a reaction index n of 1. Should it come about that the rate of growth of diffusion layers is controlled by *both* the rate of diffusion and the rate of transfer across an interface either

n greater than two. Argument based on simple rate theory, therefore, appears inadequate. If, however, phase changes should occur within the reaction layers during the reaction, disturbances in the over-all rate might be expected. Such an explanation is unorthodox, for it involves the formation of nonequilibrium phases (phases not stable at the temperature of reaction though stable at other temperatures), but it will be remembered (*vide supra*) that there is good reason to believe that a nonequilibrium phase forms in the Ag-Zn system. If changes occur in the reaction product with time, a general parabolic equation could result.

Five general types of variation in K with temperature have been noted. The Arrhen-

ius type needs no explanation. The γ and β types may be explained by transformations involving very slight and appreciable concentration changes, respectively; this may also be explained by structural changes involving only slight atom movements in the γ -type or involving large movements in the β -type. The ϵ and $\frac{1}{\epsilon}$ -types, however, require explanation.

The form of the ϵ -type and $\frac{1}{\epsilon}$ -type curves strongly suggests the occurrence of superlattice transformations. However, any explanation of this sort must involve the unlikely assumption that diffusion in the disordered state is slower than in the ordered state. In the absence of any data on diffusion in superlattices, and its change with temperature, further discussions of these curves would be fruitless.

It should be pointed out that superlattices stable at low temperatures will form more readily when grown as reaction layers than when formed from the disordered state by annealing at low temperatures; this same advantage will apply to phases stable at low temperatures only. The sensitivity of measurement of very small reaction rates will allow detection of phase or superlattice transformations at temperatures far below practically useful annealing temperatures.

If the log of phase thicknesses formed in one hour are plotted as a function of the reciprocal of absolute temperature, the Arrhenius equation is found to apply as shown in Fig. 29. It is of interest to note that while n and K of Eq. 3 vary in a complicated manner with temperature, the use of thickness attained in one hour as a rate constant yields a normal temperature variation. The latter reaction constant, which is insensitive to reaction time, indicates the necessity of an activation energy for intermediate alloy layer formation; this energy cannot, however, at the present time be assigned to any particular reaction mech-

anism. In this diagram the data on Fe-Sn were obtained from a paper by Romig and Rowland;¹⁵ the Ni-Sn data were obtained from electroplates of nickel and tin each

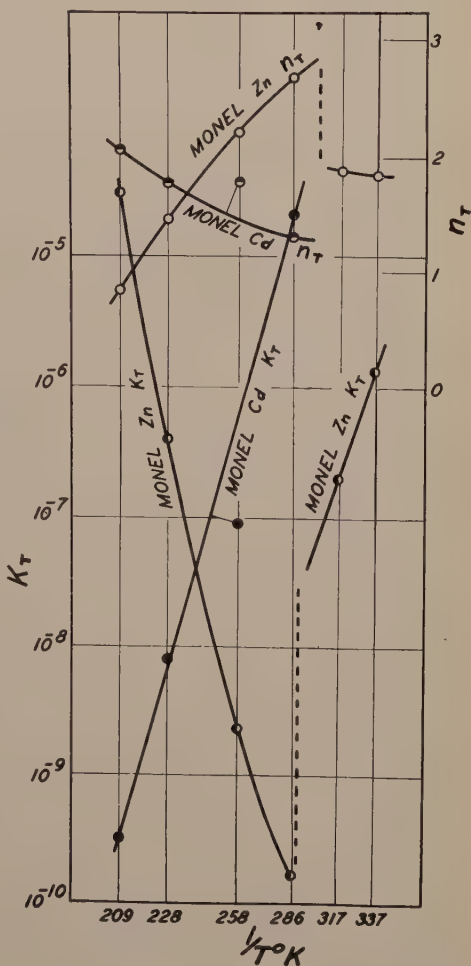


FIG. 26.—VARIATION OF REACTION INDICES n_T AND LOG OF REACTION CONSTANTS K_T FOR TOTAL DIFFUSION LAYERS IN MONEL-ZINC AND MONEL-CADMIUM SYSTEMS WITH $1/T^{\circ}K$.

0.0001 in. thick. The results obtained are summarized in Table 2. No general relation between heat of activation and melting point, or rate of reaction and atomic number could be deduced.¹⁴ In the reaction systems of Cu, Ag, and Au with Zn and

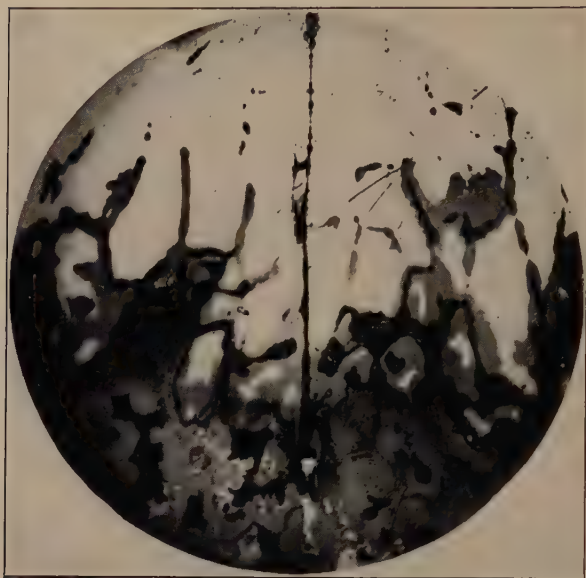


FIG. 27.—ZINC-PLATED NICKEL BLOCK CONTAINING ARTIFICIALLY PRODUCED CRACK HEATED 7 HOURS AT 379°C ., ETCHED WITH GLACIAL ACETIC ACID.

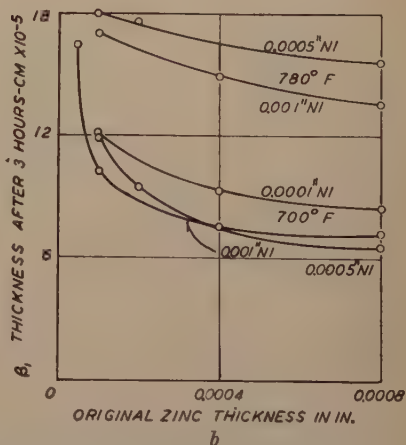
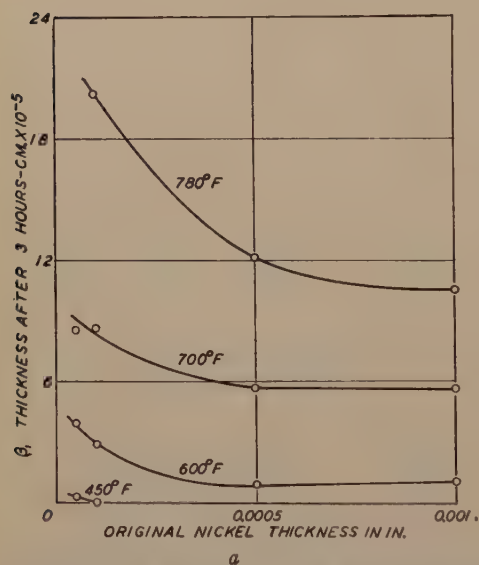


FIG. 28.—(a) VARIATION OF β_1 NiZn THICKNESS AFTER 3 HOURS DIFFUSION WITH ORIGINAL NICKEL THICKNESS; (b) VARIATION OF β_1 NiZn THICKNESS AFTER 3 HOURS DIFFUSION WITH ORIGINAL ZINC THICKNESS.

Cd, Q tends to increase with atomic number of the nobler metal. In the Zn-Fe, Fe-Co, Fe-Ni, Fe-Cu, Fe-Ag, Fe-Au systems, the heat of activation increases with atomic number to a maximum at Co, and decreases to a minimum at Cu.

SUMMARY

1. An electrolytic stripping method has been applied to the determination of phase thicknesses, and to the identification of the alloy layers in the interaction of various metals.

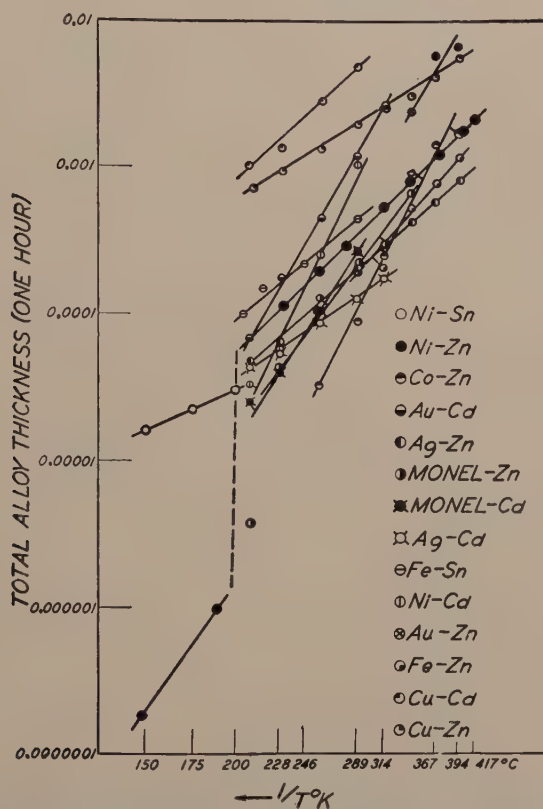


Fig. 29.—VARIATION OF TOTAL DIFFUSION LAYER THICKNESSES FORMED AFTER ONE HOUR DIFFUSION WITH TEMPERATURE (PLOTTED AS $1/T^{\circ}K$) FOR VARIOUS COMBINATIONS OF METALS.

TABLE 2.— Q and A for the Various Systems

System	Q , Cal. per Mol	A , In. per Hr.
Co-Zn.....	24,190	234,000
Fe-Sn.....	9,476	2.084
Fe-Zn.....	12,700	16.2
Ni-Zn.....	11,060	6.76
Ni-Cd.....	23,870	1,588,000
Ni-Sn.....	2,978	0.000478
Monel-Zn.....	17,500	178.3
Monel-Cd.....	11,020	6.61
Cu-Zn.....	7,050	1.079
Cu-Cd.....	10,470	57.4
Ag-Zn.....	9,900	1.42
Ag-Cd.....	7,640	0.12
Au-Zn.....	18,740	11,670
Au-Cd.....	19,830	63,100

2. The phase layers appearing in the interaction of copper, nickel, silver, and gold with cadmium and zinc and of cobalt with zinc have been identified by the preceding method.

3. Rates of formation of individual phase layers and of total reaction layers have been measured for the systems copper-zinc and copper-cadmium, nickel-zinc and nickel-cadmium, silver-zinc and silver-cadmium, Monel-zinc and Monel-cadmium, and cobalt-zinc and iron-zinc.

4. A general parabolic equation of the form

$$x^n = Kt$$

has been found generally applicable to these reactions, where X is phase thickness and t is time.

5. The constants n and K have been found to vary with temperature in at least five ways characteristic of the nature of transformations occurring at low temperatures in the various phase layers.

6. Low-temperature diffusion-layer formation is found to be quite structure-sensitive.

7. Energies of activation for various diffusion layers were determined by taking thicknesses formed in one hour of diffusion as a rate constant. No correlation was found between these energies and melting points of the various phases, atomic numbers, or other factors.

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DISCUSSION

(C. S. Barrett presiding)

F. N. RHINES,* Pittsburgh, Pa.—I should like to ask the authors whether they have

examined any cases of oxide layer growth to determine whether the simple parabolic law applies there, or whether perhaps the general law should be applied instead.

Also, I should like to propose an extension of the ideas presented in this paper. Perhaps the simple parabolic law is not vitiated by the observations made here and the general law might better be written $X^{2+N} = Kt$, where it would then be evident that the N represents some variable other than those ordinarily recognized as influencing the rate of diffusion. For example, the rate of layer growth might be partly controlled by the microstructural characteristics of the material, such as crack formation, the appearance of precipitation, and the like.

Thus, where cracks may form, we may expect sometimes to observe a more rapid diffusion of volatile substances into the cracks, promoting more rapid layer growth. In other cases the diffusing materials may not be able to jump the cracks in the alloy layers, thus delaying diffusion and resulting in a deviation from the normal rate of layer growth. Similarly, precipitates, resulting from the presence of impurities, or alloying agents might change the apparent rate of diffusion. Thus N might be a factor that would take account of changes in the microstructure that appear with time and with change in temperature.

C. S. SMITH,* Waterbury, Conn.—Have the authors any explanation for the phases above the temperature of this?

B. LUSTMAN (author's reply).—A search of the literature was made in an attempt to find data that would be suitable for reploting in the manner shown in the paper. Only two sets of such data (both on the scaling of iron) were found: (1) by Heindlhofer and Larsen,¹⁶ and (2) by Portevin, Pretet and Jolivet.¹⁷ Both sets of data revealed that the *general*, rather than the *simple*, parabolic equation is obeyed. The reaction index n varies with temperature between 1.5 and 3 and shows a minimum at the A_3 temperature; corresponding variations are found in the reaction constant K . It should be

* Research Metallurgist, American Brass Co.

¹⁶ Heindlhofer and Larsen: *Trans. Amer. Soc. Steel Treat.* (1933) **21**, 865.

* Research Metallurgist, Assistant Professor of Metallurgy, Carnegie Institute of Technology.

¹⁷ Portevin, Pretet and Jolivet: *Jnl. Iron and Steel Inst.* (1934) **130**, 219.

noted that both Heindlhofer and Larsen and Dunn¹⁸ recognized the validity of a general parabolic equation, $X^n = Kt$; however, its applicability they attributed to accidental disturbances of the normal course of scaling rather than to a characteristic of the formation of intermediate alloy layers.

As Dr. Rhines points out, the data presented in this paper in no way invalidate the diffusion equations, nor were the results intended to be so interpreted. The validity of the simple parabolic equation requires that the diffusion coefficient, the concentration gradient, the mechanical and crystallographic structures of the diffusion layer remain constant with time; in the process of formation of inter-

mediate alloy layers there exists no *a priori* reason for assuming such conditions. It should be pointed out that not only microstructural changes such as those listed by Dr. Rhines or crystallographic changes as suggested in the paper may be responsible for deviations from the simple parabolic equation; for instance, change with time of the concentration gradient, a change that would appear very likely to occur, would provide the general diffusion equation for the growth of the diffusion layer.

The explanation sought by Dr. Smith of the appearance of phases in the diffusion layer at diffusion temperatures above which the phase is stable possibly rests in greater ease of nucleation of the unstable phase as compared with the stable phase.

¹⁸ Larsen and Dunn: *Jnl. Inst. Metals* (1931) **46**, 25.

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